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Assessment of water quality in urban and rural stormwater runoff

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ASSESSMENT OF WATER QUALITY IN URBAN AND RURAL STORMWATER RUNOFF

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ABSTRACT

TITLE: Assessment of Water Quality in Urban and Rural Stormwater Runoff

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Land uses within the San Francisquito Creek watershed range from high density urban to typical rural uses. To improve the Creek's health, it is beneficial to determine where specific pollutants are originating.

The objectives of this study were to compare nutrient and pesticide inputs between urban and rural land uses, compare sites to a reference site, and determine if a relationship exists between pollutant concentration and percent impervious cover. Stormwater runoff was measured for nitrate, nitrite, orthophosphate, ammonia, diazinon, and chlorpyrifos from 14 outfalls during 3 storm events.

Results indicate that diazinon is more widely used in the lower watershed where land uses with high imperviousness dominate. Chlorpyrifos was negatively correlated with imperviousness, indicating that land uses typical of the rural watershed are contributing more of the pesticide than the urban area. Nitrate, nitrite, and orthophosphate concentrations at sites draining a tree farm were significantly higher than the reference site.

Key Words: water quality, nutrients, organophosphate pesticides, impervious, San Francisquito Creek

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National Level

Nonpoint source (NPS) pollutants, which originate from diffuse or non-specific sources, have been recognized as major sources of water quality degradation in surface waters in the United States (Wong, Strecker, and Stenstrom 1997; Tsihrintzis and Hamid 1997; and Gilliland and Baxter-Potter 1987). NPS pollutants, such as nutrients and sediment, originate from human-induced stresses in the watershed including agriculture, grazing, urbanization, roads, and deforestation. Not only do these land uses produce pollutants, but they also reduce the filtration ability of natural ecosystems. Filtration is reduced by covering soil with impervious surfaces and reducing native vegetation that can capture and remove some pollutants.

Increased impervious coverage results in a decrease in the amount of stormwater able to percolate into the soil. In urbanized areas, precipitation running off roofs, sidewalks, parking lots, and lawns flows into streets until it reaches a stormdrain where it enters the creek. Stormwater runoff carries many of the pollutants that settle on these surfaces into nearby creeks. Significantly elevated pollutant concentrations in runoff may be related to the amount of impervious surface coverage within the drainage area from which the runoff originates. The amount of impervious coverage is dependent on the type and percentage of land uses.

Changes within a watershed due to urbanization result in accelerated stormwater runoff and increased pollutant loading in streams (Yu 1982). According to the Clean Water Action Plan (1998), polluted runoff is the primary source of water quality degradation in the United States. The Plan also reports that urban runoff (including storm sewers) is the fifth leading cause of water quality degradation in rivers. Runoff may contain such pollutants as nutrients (nitrites, nitrates, phosphates, and ammonia), heavy metals (lead, zinc, copper, mercury, cadmium), hydrocarbons, pesticides, and particulates (Hunter et al. 1982). Wagner and Geiger (1996) state that stormwater discharges into urban creeks result in both recreational and ecological impairment.

Land uses will also affect the quantity and quality of runoff entering streams (City of Greensboro 1996). Numerous studies have evaluated the quality of stormwater runoff entering the nation's urban streams. Many of these studies focus on a particular pollutant. Hunter et al. (1982) and Charcklis and Wiesner (1997) measured heavy metal loads in a single watershed. Both studies found an increase in heavy metal concentrations, especially zinc, lead, copper, and nickel, during storm events. Nutrients are also widely monitored in streams draining both urban and rural watersheds (Kluesener and Lee 1974; Boyd 1996; Nelson, Cotsaris, and Oades 1996). Boyd (1996) found increased levels of nitrates from sites draining agricultural land uses. A study of the San Joaquin and Sacramento Rivers, by Kuivila and Foe (1995), showed that stormwater runoff transported elevated concentrations of pesticides to the rivers from adjacent land uses.

Local Level

The San Francisco Bay (Bay) and Delta together form a 1,600 square-mile (4,160 square kilometer) estuary, the largest estuary on the West Coast. The estuary drains 40 percent of California and receives 47 percent of the state's total runoff (San Francisco Estuary Project 1997). Along with runoff, however, come numerous pollutants originating from extensive agricultural practices in the Central Valley and the urbanized metropolitan Bay Area. Widespread urban sprawl in the Bay Area has significantly decreased the amount of natural habitat, particularly riparian zones, in the watershed. Riparian habitat slows runoff and allows infiltration of pollutants to occur, decreasing pollutant loads to surface waters. In California, nearly 90 percent of the state's original 921,000 acres of riparian habitat has been lost (Jensen, Torn, and Harte 1993). At a local level, over 200 miles of creeks on the valley floor of Santa Clara County have been altered through widening, realigning, or channelizing (Santa Clara County General Plan 1990).

Section 303(d) of the Clean Water Act requires states to identify waters not meeting state water quality standards. The impaired waters must be ranked by priority and submitted to the Environmental Protection Agency every 2 years (Ruffolo 1999). The current list for California includes 509 impaired waters (U.S.

Environmental Protection Agency (1999a). A map of the impaired waters of California is shown in Figure 1.

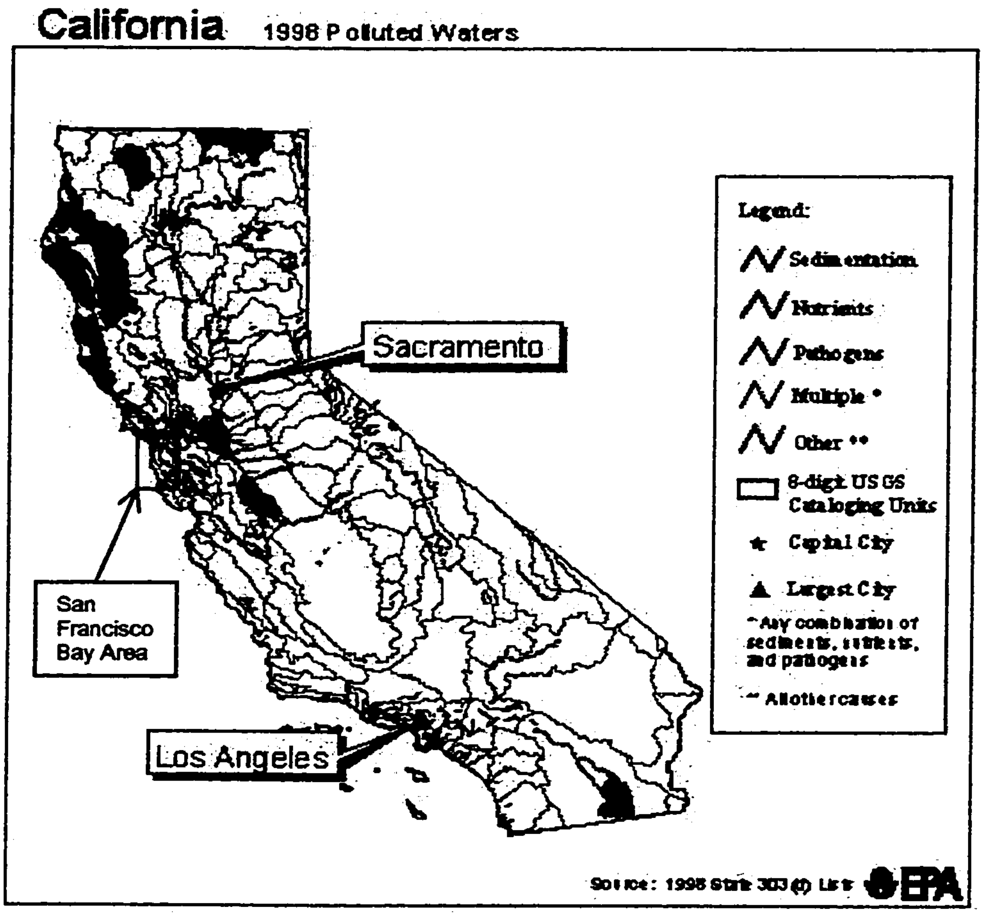


Figure 1: Water bodies listed impaired in California in accordance with the Clean Water Act, Section 303(d) as well as major causes of impairment.

Included in the list of impaired waters are the South San Francisco Bay and the urban creeks flowing into the South Bay. The Bay has been listed as impaired because of elevated levels of pollutants including mercury, copper, nickel, and diazinon. All urban creeks draining into the South Bay have been listed impaired for diazinon. Many urban creeks in the South Bay basin have been listed for other pollutants. San Francisquito Creek, for example, has been listed for sediment/siltation and diazinon (U.S. Environmental Protection Agency 1998).

For impaired water bodies, the Clean Water Act also requires the state or the EPA to calculate a Total Maximum Daily Load, or TMDL. A TMDL is defined as "the maximum amount of a pollutant that a water body can receive and still meet water quality standards, and an allocation of that amount to the pollutant's sources. A TMDL is the sum of the allowable loads of a single pollutant from all contributing point and nonpoint sources." (U.S. Environmental Protection Agency 1999b). TMDLs must be calculated for both sediment and diazinon for San Francisquito Creek.

San Francisquito Creek (Figure 2), located on the boundary of San Mateo and Santa Clara Counties, drains an area of 43 square miles (112 square kilometers) and originates on the east slope of the Santa Cruz Mountains (United States Geological Survey 1995). The current condition of the Creek and watershed is of concern because it flows directly into the South San Francisco Bay and provides aquatic and terrestrial habitat to plant and animal species.

Several rare species use this watershed including threatened steelhead trout (*Salmo gairdnerii gairdnerii*) that return to the creek to spawn (San Mateo County General Plan 1986), the California red-legged frog (*Rana aurora draytonii*), a federally-listed threatened species (Seymour pers. comm.), and the western pond turtle (*Clemmys marmorata*), a federal species of concern (California Department of Fish and Game 1999).

The San Francisquito Creek watershed encompasses several different jurisdictions, making land management efforts a difficult and challenging process. These jurisdictions include two counties, Santa Clara and San Mateo, the cities of Palo Alto, East Palo Alto, Menlo Park, Atherton, Ladera, Woodside, Portola Valley, and unincorporated areas. Stanford University and Stanford Golf Course are also located within the watershed and Stanford Management Company owns a fair amount of land adjacent to the Creek that the Company leases for various uses such as a commercial tree farm and horse training and boarding facilities.

In 1993, a Coordinated Resource Management and Planning (CRMP) committee was formed to assist the numerous stakeholders in managing the watershed in order to preserve and restore the creek while respecting jurisdictional rights. A major objective of the CRMP committee is to collaborate with representatives from jurisdictions and stakeholders to develop a watershed plan for San Francisquito Creek (Coordinated Resource Management and Planning Committee 1997).

The downstream portion of San Francisquito Creek, or the lower watershed, consists primarily of urbanized areas with high percentages of impervious surface coverage, increasing the potential for high pollutant loading. The upper watershed is rural with much less land covered by impervious surfaces. Current types of land uses located within the watershed include a golf course, residential housing, horse stables (public and private), trails, small ranches, an airport, open-space, and small-scale agriculture. Stretches of stream bank have been covered with concrete, removing the riparian habitat in those areas. Paved roads with high traffic volumes parallel the creek in close proximity throughout the watershed. The combined factors of adjacent land uses and increased impervious surface area can result in cumulative effects that may significantly degrade the riparian and aquatic environment, as there is decreased filtering by vegetated buffer strips and increased surface runoff.

Understanding the current conditions of San Francisquito Creek is imperative for: 1) predicting the effects of future land use and management decisions, 2) making recommendations to land use planners, 3) obtaining baseline data to determine what management activities have been successful, 4) planning, implementing, and monitoring restoration projects, 5) conducting cumulative impact assessments, and 6) improving current water quality impairments. Proper land management decisions are essential for improving the quality of the creek and for reducing impacts to the San Francisco Bay. Analyses such as this can also identify opportunities for restoration that will benefit creek health. Predicting the potential effects of future land use changes can allow for implementation of best management practices (BMPs), help in developing adequate mitigation measures, or identify opportunities to limit the impacts that occur.

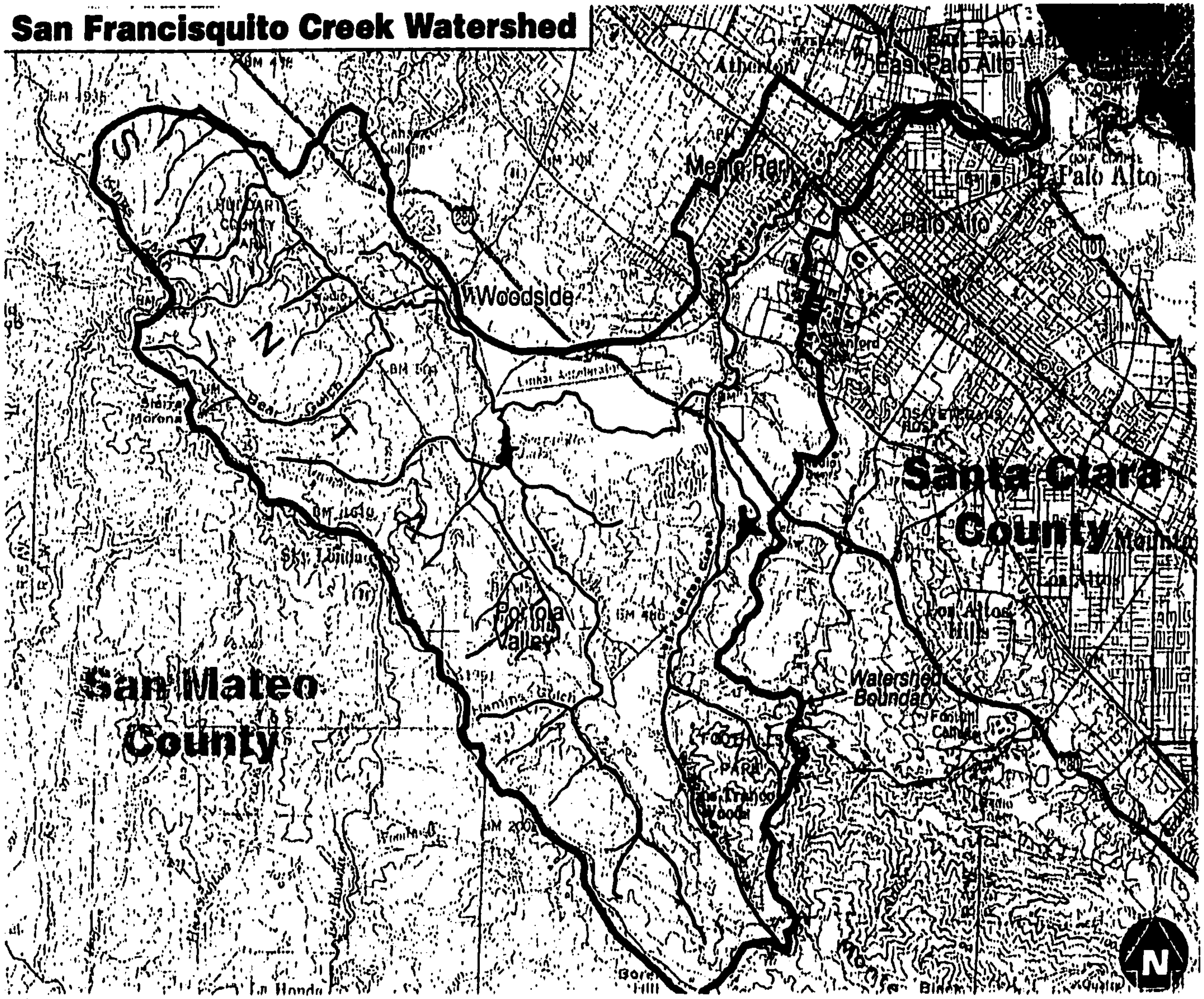


Figure 2: San Francisquito Creek Watershed

Source: Coordinated Resource Management and Planning committee (1997)

OBJECTIVES

The primary focus of this thesis was to evaluate nutrient and pesticide concentrations in stormwater runoff reaching San Francisquito Creek via stormdrains. Nutrients and sediment tend to originate from rural areas while pesticides (particularly diazinon) and heavy metals tend to originate in urban areas (Bruhns pers. comm.). Local experts agree (Barbash pers. comm.; Sarmiento pers. comm.) that pesticides (in particular diazinon and chlorpyrifos) and nutrients are important contaminants to consider because of their extensive use on the lands bordering the Creek and their effects on aquatic organisms in the Creek and Bay. In addition, San Francisquito Creek has been listed as impaired for diazinon and sediment/siltation by the U.S. Environmental Protection Agency under Section 303(d) of the Clean Water Act.

With a better understanding of the concentrations and sources of these pollutants within the watershed, proper land management practices can be focused on specific areas and land uses. Implementation of restoration projects, best management practices, and other land management methods can reduce the impacts of current and future land use activities.

This study was designed to assess nutrient and pesticide concentrations in stormwater runoff reaching San Francisquito Creek via stormdrains in order to determine how land uses are contributing to pollutant inputs. The specific research questions this study addresses were:

1) What concentrations of nutrients and pesticides enter the creek from urban and rural land uses during storm events?

2) Is there a significant difference in pollutant concentrations originating from urban and rural land uses?

3) Is there a significant difference in pollutant concentration between sites and a reference site?

4) Is there a relationship between pollutant concentrations and the percentage of outfall drainage area covered by impervious surfaces?

5) What BMPs and/or management methods might be effective in reducing pollutant inputs?

RELATED RESEARCH

Nonpoint sources contribute significantly to the contaminants present in stormwater runoff. The type of contaminants present are determined primarily by the type of land use where the runoff originates and through which it passes before entering a water body. Other factors affecting the quality and quantity of runoff are rainfall, geology, vegetation type, topography, traffic volume, and the number of days between storms (Tsihrintzis and Hamid 1997).

Imperviousness and Water Quality

The percent of impervious cover (imperviousness) within a drainage basin is also an important factor that affects the amount of runoff entering a stream. Impervious surfaces include roads, roofs, parking lots, sidewalks, and driveways. High percentages of impervious coverage result in a greater accumulation of pollutants between storms and a decreased amount of precipitation infiltrating into the soil. After accumulating on concrete or asphalt, pollutants are washed by storm events into the nearest water body (Schueler 1994). According to the San Mateo County General Plan (1986), impervious surfaces have increased the amount of runoff entering waterways in San Mateo County "resulting in poor water quality and impaired vegetative, fish and wildlife habitats."

Imperviousness has been shown to be useful as an indicator to measure the impacts of land development on stream health (Schueler 1994). Numerous studies, some of which are discussed below, relate impervious surface coverage to degraded water quality in streams (Schueler 1994; Arnold and Gibbons 1996; Eisenberg, Olivieri, and Associates, Inc. 1996; Booth and Jackson 1997). Schueler (1994) reports that numerous researchers have found similar conclusions when drawing links between urbanization and stream degradation. Although a variety of methods have been used in different geographic locations, studies conclude that stream degradation occurs at levels of imperviousness ranging from 10 to 20 percent (Booth and Jackson 1997; Eisenberg, Olivieri, and Associates 1998; Schueler 1994; Schueler 1996).

To identify specific sources of urban pollutants, Bannerman et al. (1993) sampled stormwater runoff from different surfaces in Madison, Wisconsin. These surfaces were primarily impervious such as streets, roofs, driveways, and parking lots. The exception was residential lawns. This research showed that streets contributed the highest concentration of pollutants, including nutrients, metals, and suspended solids. Lawns contributed the highest concentrations of phosphorus. Roofs produced the highest concentrations of zinc.

Booth and Jackson (1997) discuss the difference between total impervious area (TIA) and effective impervious area (EIA). Total impervious area includes all impervious surfaces such as concrete, asphalt, and rooftops. Effective impervious area, which is much more complicated and difficult to measure, is defined as, "the impervious surfaces with direct hydraulic connection to the downstream drainage (or stream) system." In other words, any impervious area that drains onto a pervious area is not included when measuring effective imperviousness.

Booth and Jackson (1997) found that at approximately 10 percent effective impervious cover, streams in western Washington show "demonstrable, and probably irreversible, loss of aquatic-system function." Lower levels of effective impervious area result in significant degradation in sensitive water bodies. The authors warn that these values do not indicate thresholds of urban development as degradation occurs at very low development levels.

Eisenberg, Olivieri, and Associates, Inc. (1998) classified local creeks as sensitive, impacted, or non-supporting depending on the percent (total) impervious coverage in the watershed. The percentages used, which were derived from Schueler (1994; 1996) are 0 to 10 percent for sensitive, 11 to 25 percent for impacted, and 26 to 100 percent for non-supporting. In their study, San Francisquito Creek has an average percent impervious coverage of 22 percent, ranking the creek as impacted.

In later work done by Eisenberg, Olivieri, and Associates, Inc., for the Santa Clara Basin Watershed Management Initiative (2000), the authors calculated the amount of total impervious area in acres of each land use type and the total percentage of imperviousness for the San Francisquito Creek watershed (21 percent). This result is similar to the results of their previous work that showed an average percent impervious cover of 22 percent. Table 1 shows that moderate-density residential land uses comprise the most impervious coverage in the watershed (9.3 percent) followed by high-density residential (6.0 percent).

Table 1: Acres of Impervious Cover by Land Use Type in the San Francisquito Creek watershed. (Source: Santa Clara Basin Watershed Management Initiative 2000)

LAND USES	IMPERVIOUS ACRES	PERCENTAGE OF WATERSHED IMPERVIOUSNESS
Moderate-Density Residential	2551.3	9.3
High-Density Residential	1642.1	6.0
Public, Quasi-Public	531.8	1.9
Commercial	470.9	1.7
Transportation, Communication	195.1	0.7
Forest	122.6	0.5
Rangeland	86.5	0.3
Urban Recreation	65.0	0.2
Heavy Industrial	16.7	0.1
Agriculture	12.2	<0.05
Low-Density Residential	1.7	<0.05
Utilities	1.2	<0.05
Vacant, Undeveloped	4.0	<0.05
Wetlands	0.5	<0.05
TOTAL	**5701.6**	**20.8**

<u>Nutrients</u>

Excess nutrients in streams may originate from both point and nonpoint sources (Cullen 1980; Puckett 1995) and are a recognized concern in the United States (Nelson, Cotsaris, and Oades 1996). Gianessi and Peskin (1981) reported that 87 percent of phosphorus and 88 percent of nitrogen entering surface waters in the United States originate from nonpoint sources. According to Pat Showalter (pers. comm.) of the Coordinated Resource Management and Planning (CRMP) committee for San Francisquito Creek, nutrients are a primary concern for San Francisquito Creek because of the large number of confined animal stables adjacent to the creek.

Nutrients can originate from both urban and rural land uses and are transported to streams in stormwater runoff. Anthropogenic sources of nutrients from urban land uses include household fertilizers, animal waste, soil erosion, yard clippings (Cullen 1980), as well as wet and dry deposition from the atmosphere, construction activities, and garbage (Cullen 1980; Puckett 1995). Rural sources include pasture, agriculture, forests (Cullen 1980), and animal waste (Liu et al. 1997). Nutrient concentrations can vary throughout the year due to changes in precipitation and streamflow and to differences in application practices of manure and fertilizer (United States Geological Survey 1999).

A watershed containing one or more of these land uses may have elevated nutrient concentrations in the rivers and streams draining them resulting in eutrophication of the water body (Nelson, Cotsaris, and Oades 1996; Boyd 1996; Tzihrintzis and Hamid 1997). Eutrophication is defined as the process in which nutrients increase the growth of aquatic plants such as phytoplankton, periphyton, and algae. This excess growth can be harmful to aquatic organisms by blocking sunlight and depleting oxygen levels resulting in fish kills (Dunne and Leopold 1978; Boyd 1996). Nitrogen and phosphorus are the nutrients primarily responsible for eutrophication problems (Boyd 1996; Sharpley and Menzel 1987; Cullen 1980). In addition, phosphorus and nitrogen may also have "subtoxic effects on aquatic organisms" (Ellis 1986).

Nitrogen. Under natural conditions, nitrogen is present in surface water as nitrate, nitrite, ammonium, and organic nitrogen. All forms of nitrogen are part of the nitrogen cycle and are able to biochemically convert from one form to another. Nitrate (NO_3^-) is a primary nutrient for growth in plants and is a required nutrient for algae. Nitrates are formed when bacteria converts organic nitrogen to nitrites and then to nitrates (Stednick 1991). Anthropogenic sources of nitrates include animal waste and fertilizer. Runoff from farms, lawns, animal feedlots, and dairies can contain high concentrations of nitrate (Mitchell and Stapp 1994).

Throughout the literature, nitrites (NO_2^-) seem to be the nutrient that is analyzed the least. This may be due to the relatively quick conversion of nitrites to nitrates by bacteria in the water. In a study conducted by the United States Geological Survey (1999), the sum of nitrites and nitrates were reported as nitrate. Nitrites are still able to contribute to eutrophication and can have toxic effects to fish. MacDonald, Smart, and Wissmar (1991) report that nitrites can be toxic to fish at levels as low as 0.05 mg/l.

Ammonia (NH_3) becomes present in water through the natural process of oxidization. Bacteria break down large protein molecules in dead plants and animals to produce ammonia. Ammonia also originates from animal excrement and is commonly found in chemical fertilizers. While ammonia is a nutrient that is a concern due to eutrophication, high concentrations can be toxic to aquatic organisms. Concentrations as low as 0.08 mg/l are toxic to some aquatic invertebrates and fish (MacDonald, Smart and Wissmar 1991). Trout are particularly sensitive to un-ionized ammonia (United States Geological Survey 1999).

Phosphates. Phosphates are the most common form of phosphorus found in natural waters and are generally reported as orthophosphate (PO_4^{3-}). Orthophosphates are produced from the dissociation of phosphoric acid (Stednick 1991). Orthophosphates originate from animal waste, industrial waste, and fertilizers. Like nitrogen, phosphorus is essential for plant growth and metabolic reactions. Under natural conditions, phosphorus acts as the limiting factor for plant growth as it is found in low concentrations (Mitchell and Stapp 1994). Orthophosphates constitute the majority of dissolved phosphates, which can be readily assimilated by aquatic plants and promote eutrophication. Other forms of phosphate tend to bind to particles making them less mobile through soil (United States Geological Survey 1999).

Pesticides

While pesticides are designed to eliminate unwanted insects or target organisms, they are generally toxic to non-target organisms as well (Brown 1980). Increased levels of pesticides can cause fish kills, reduce reproductive rates, and can alter fish behavior (Hunt and Linn 1970). Pesticides can also be harmful to birds as they can cause thinning of eggshells and decreased reproductive rates (Stickel and Rhodes 1970). Pesticides can be transported via air or water and settle in sediment (Dunne and Leopold 1978).

Organochlorines such as DDT, heptachlor, aldrin, and dieldrin were used extensively throughout the world until the 1970s when most uses were banned or restricted in the United States. Organochlorine pesticides are highly toxic and can persist in the environment for decades (Larson, Capel, and Majewski 1997). In a seven year study (1991-1997) conducted by the United Stated Geological Survey (1999), organochlorine compounds were the pesticides detected most often in fish and sediment. Biomagnification occurs as pesticide concentrations increase when consumed by predators in the food chain (Dunne and Leopold 1978).

Organophosphates, such as diazinon, chlorpyrifos, and parathion have been widely used since the 1960s and 1970s when organochlorines were restricted and banned (Larson, Capel, and Majewksi 1997). Some organophosphates, such as malathion and parathion, are more toxic than organochlorines but they are less persistent in the environment (Dunne and Leopold 1978). Although these compounds have short half-lives, their presence in runoff may threaten surface waters. Organophosphates are slightly to highly toxic in birds, moderately to highly toxic in fish, and highly toxic to aquatic invertebrates (Kamrin 1997).

Pesticides are of concern in San Francisquito Creek because of their widespread use in agriculture and household and commercial landscaping. Land uses in the San Francisquito watershed that may be significant sources of pesticide contamination include golf courses, Stanford University and residential lawns, residential and commercial landscaping, tree farms, and agriculture. Common organophosphate pesticides used in Santa Clara County are chlorpyrifos, glyphosate, diazinon, acephate, malathion, and dimethoate (Cooper 1996). The two pesticides of greatest concern for San Francisquito Creek are diazinon and chlorpyrifos (Sarmiento pers. comm.).

Diazinon. Diazinon is a common organophosphate insecticide used in both households and agricultural settings and is an active ingredient in over 200 California Department of Pesticide Regulation registered products (Katznelson and Mumley 1997). Trade names of this product include Basudin, Dazzel, Gardentox, Kayazol, Knox Out, Nucidol, and Spectracide. It is also sold as a formula with other pesticides. In residential areas, it is used to control cockroaches, silverfish, ants, and fleas. It is also used for controlling leaf-eating insects on rice, fruit trees, corn, potatoes, and horticultural plants in both household gardens and commercial farms. It comes in various forms including dusts, sprays, and granules (National Pesticide Telecommunications Network 1998). Diazinon can be found in pest strips and is used by veterinarians to control fleas and ticks (Kamrin 1997).

Diazinon is highly toxic to birds, fish, and aquatic invertebrates. In animals, the toxicity of this pesticide is due to the conversion of diazinon to diazoxon, a cholinesterase inhibitor. Cholinesterase is an enzyme needed for proper functioning of the nervous system. The half-life of diazinon in animals is approximately 12 hours (Kamrin 1997).

Birds are significantly more susceptible to diazinon poisoning than other wildlife. The LD50 for birds ranges from 2.75 mg/kg to 40.80 mg/kg (Kamrin 1997). Diazinon is also toxic to fish although warm water fish are more resistant to diazinon than cold water fish (Kamrin 1997). The LC50 for rainbow trout, a cold water fish, is 2.60 to 3.20 mg/l. The LC50 for *Ceriodaphnia dubia* within 48 hours of exposure ranges from 300 to 500 ng/l (Katznelson and Mumley 1997). The 4 day average diazinon standard is 40ng/l per the National Toxics Rule (57 FR 60848) (Menconi and Paul, 1994a).

Diazinon has a low persistence in soil with a half-life of 2 to 4 weeks (Kamrin 1997) and a foliage half-life of 4 days (National Pesticide Telecommunications Network 1998). Diazinon has a low potential to move from the soil to groundwater, although it has a high potential to be transported from soil and into runoff (Larson, Capel, and Majewski 1997). In water, diazinon can take up to six months to degrade to one half of its original concentration (Kamrin 1997).

<u>Chlorpyrifos.</u> Chlorpyrifos is an organophosphate insecticide used to control cutworms, corn rootworms, cockroaches, grubs, flea beetles, flies, termites, ants, and lice. In rural areas it is used in agricultural practices to control insects on grain, cotton, fruits, nuts, and vegetable crops and is registered for use in horse stables and farm buildings. In residential areas it is used on lawns

and ornamental plants, as well as around homes and commercial buildings. It is also the active ingredient in flea and tick dips for household pets. Chlorpyrifos is available in granules, wettable and dustable powders, and emulsifiable concentrates (Extoxnet 1996). Trade names for this insecticide include Brodan, Detmal UA, Dowco 179, Dursban, Empire, Eradex, Lorsban, Paqeant, Piridane, Scout, and Stipend (Kamrin 1997).

Chlorpyrifos is moderately to highly toxic to birds and can result in reduced egg production. The oral LD50 in birds ranges from 8.4 to 32.0 mg/kg (Extoxnet 1996). Chlorpyrifos is highly toxic to freshwater fish, aquatic invertebrates, and estuarine and marine organisms. The 96-hour LC50 for rainbow trout is 0.009 mg/l and 0.331 mg/l in fathead minnow. Research also shows decreased survival rate and growth and increased deformities in fathead minnows exposed to 0.002 mg/l of Dursban for a 30-day period (Kamrin 1997). The National Toxics Rule (57 FR 60848) 4 day average chlorpyrifos standard is 5.6 ng/l (Menconi and Paul 1994b).

The half-life of chlorpyrifos in soil ranges from 60 to 120 days, but depending on soil type and climate can persist for over one year. In water, the persistence of chlorpyrifos varies depending if the insecticide is in powder or granular form. Initially, high concentrations will be present if wettable powders are used, but those levels decrease when the powder adheres to sediment and organic matter. When in the granular form, the insecticide persists for a longer period of time (Kamrin 1997).

Quantitative Methods

Numerous studies have measured pollutant loads to urban streams from stormwater runoff. In their study conducted in New Jersey and Pennsylvania, Hunter et al. (1982) list three methods to estimate the level of pollutants in urban runoff. These methods are: 1) sample stormwater from a sewer draining the study area; 2) sample directly from a stream receiving the stormwater before, during, and after a storm event; and 3) sample before, during, and after a storm and above and below the study area. Hunter et al. (1982) chose to collect samples directly from storm sewers due to the simplicity of this method.

Several studies have monitored nutrient levels in urban runoff (Kluesener and Lee 1974; Boyd 1996; Nelson, Cotsaris, and Oades 1996). Kluesener and Lee (1974) measured nutrient concentrations (nitrogen and phosphorus) from storm sewers draining an urbanized area in Madison, Wisconsin. An automatic sampler was used to collect runoff samples during the first flush of 17 storm events and then at five to ten minute intervals thereafter. An automatic sampler was chosen so discrete samples would be collected immediately at the start of a storm.

Kluesener and Lee (1974) found that the highest concentration of nutrients occurred at the beginning of the rainfall event then decreased and remained constant. The authors list three reasons for this trend. First, rain itself contains the highest amount of nutrients at the beginning of a storm. Second, the intensity of rainfall is greatest at the beginning of an event. Third, and probably most significant, the majority of contaminants are flushed at the start of the storm. Although most authors agree that pollutant loads will increase as the time between storms increases, one study, by Hunter et al. (1982), did not find this result.

Boyd (1996) measured orthophosphate and nitrate concentrations from nine fixed sites to determine the distribution of these pollutants in streams draining Central Nebraska Basins. Samples were tested for nitrate, nitrite, ammonia, phosphorus, and orthophosphate using a colorimeter. The study found that nitrate levels were highest where agricultural land uses dominated and during winter months. Ninety percent of the samples tested for nitrate were below the U.S. Environmental Protection Agencies maximum contaminant level of 10 milligrams per liter for public drinking water supplies. Boyd (1996) states that this level is generally used to compare water quality levels whether or not the water source is for public use. Orthophosphate levels were relatively low at all sites.

In another study monitoring nutrient levels, Nelson, Cotsaris, and Oades (1996) analyzed concentrations in runoff from two basins where grazing is the primary land use. The samples were collected when flow reached a specific threshold level. Discharge and mean concentrations were used to estimate annual load. The study found that nitrogen, phosphorus, and organic carbon were present at levels high enough to cause eutrophication.

The United States Geological Survey (USGS) (1999) conducted an intensive, 7-year study of nutrient and pesticide concentrations in surface and ground water throughout the United States. Water samples were collected from 212 stream sites for nutrient analysis and 65 stream sites for pesticide analysis. Samples were collected throughout the year and during both low and high flow conditions. In over half of the streams sampled, concentrations of total nitrogen and total phosphorus exceeded national background concentrations. The findings also demonstrate that nutrient enrichment occurred in small streams in watersheds containing a large amount of agricultural or urbanized land uses.

In the same study, the USGS also monitored pesticide concentrations of 83 target compounds and found at least one pesticide in nearly every sample collected from streams. Pesticides were detected in both agricultural and urban areas of the United States. In urban areas, concentrations of some pesticides often approached or exceeded water quality guidelines. Insecticides that are typically used in urban areas for household and commercial uses frequently occurred at levels of concern for aquatic life. The report states that this may be a significant barrier to urban stream restoration.

Katznelson and Mumley (1997) prepared a report for the California State Water Resources Control Board and the Alameda Countywide Clean Water Program that compiled diazinon water quality data and aquatic toxicity data from San Francisco Bay and Central Valley urban creeks and stormwater discharges. Toxicity Identification Evaluation was performed in the Castro Valley Creek watershed, Crandall Creek watershed, and in the Sunnyvale East Channel watershed in Santa Clara County. The toxicity procedures identified diazinon as the major cause of toxicity in all three watersheds. The report summarizes the findings of numerous other studies that have been performed in the San Francisco Bay Area that have detected diazinon concentrations in stormwater and creeks.

Lopes and Fossum (1995) collected 14 first flush stormwater samples from six drainage basins to measure concentrations of oil and grease, suspended solids, chlorine, ammonia, hardness, trace metals, and organophosphate pesticides. The authors' objective was to "identify and minimize sources of toxicants." The drainage basins sampled contained residential, commercial, and industrial land uses. Stormwater samples collected from residential and commercial land uses contained the most toxic constituents. The authors conducted toxicity tests on fathead minnows (*Pimaphales promelas)* and water fleas (*Ceriodaphnia dubia)*. The results of this study showed that stormwater from these drainage basins contained levels of oil and grease, pesticides, trace metals, and ammonia that could be detrimental to water quality. Stormwater was found to be more harmful to fathead minnows than water fleas.

A range of collection methods exists and there is some controversy about which methods provide the best data. For example, authors dispute whether automatic or grab sampling is best. The number of samples to collect per storm event in order to achieve statistically valid results is also a source of debate.

The methods chosen for this thesis study were derived from research conducted by the City of Greensboro, North Carolina Department of Environmental Services (1996) and a volunteer monitoring project conducted by the Alameda Countywide Clean Water Program (1999). These methods were chosen because they are usable by both municipalities and citizen volunteer groups. The City of Greensboro methods provided statistically valid and reliable results that were used for regulatory purposes. The City of Greensboro monitored stormwater runoff from urban nonpoint sources as part of their National Pollutant Discharge Elimination System (NPDES) municipal stormwater permit. The purpose of their monitoring program was to characterize discharges from different land use types, including residential, industrial, agricultural, and undeveloped. Staff manually collected both a first flush grab sample and a time-weighted composite of runoff from 7 outfalls, each site representing a different land use. Samples were analyzed for an extensive list of pollutants to satisfy the NPDES requirements (City of Greensboro 1996).

The Alameda Countywide Clean Water Program used volunteers to collect stormwater samples from outfalls to measure diazinon concentrations entering San Leandro Creek. Volunteers collected multiple grab samples during each storm event from 10 outfalls and also took samples directly from the creek near each outfall. Samples were analyzed for diazinon using a procedure called enzyme-linked immunosorbent assay, or ELISA. The ELISA method utilizes antibodies attached to plastic microwells. These antibodies are very specific in their ability to recognize and bind to an antigen and therefore pull the diazinon and chlorpyrifos molecules out of the sample. The amount of diazinon and chlorpyrifos molecules is calculated using a calibration curve prepared with standard solution of known concentration (Alameda Countywide Clean Water Program 1999).

WATERSHED DESCRIPTION

The San Francisquito watershed drains an area of 43 square miles (112 square kilometers or 24,320 acres) and is the largest watershed in San Mateo County, California that drains into the San Francisco Bay (San Mateo County General Plan 1986). San Francisquito Creek originates on the east side of the Santa Cruz Mountains (latitude 37°25'24", longitude 122°11'18"), downstream of Searsville Lake. The watershed encompasses several cities (East Palo Alto, Palo Alto, Menlo Park, Woodside, Ladera, Atherton, and Portola Valley) and the creek flows along the border of San Mateo and Santa Clara Counties eventually reaching the South San Francisco Bay south of the Dumbarton Bridge (United States Geological Survey 1995). Major tributaries of San Francisquito Creek include Los Trancos Creek, Corte Madera Creek, West Union Creek and Bear Creek (Figure 2). The study area for this thesis includes San Francisquito Creek downstream of Searsville Dam to the San Francisco Bay and the tributary Bear Creek.

San Francisquito Creek is a fourth order stream (Santa Clara Basin Watershed Management Initiative 2000) and is characterized by pool and riffle habitats. The California Regional Water Quality Control Board (1995) lists the beneficial uses of the creek as fish migration, fish spawning, warm and cold fresh water habitat, wildlife habitat, and recreation. Beneficial uses are defined as "...the resources, services, and qualities of aquatic systems that are the ultimate goals of protecting and achieving high water quality" (California Regional Water Quality Control Board 1995).

Natural communities and human land uses occur within the watershed. The upper portion of the watershed includes significant amounts of natural habitat and rural or non-urban land uses including small ranches, tree farms, horse stables, rural residential, and Jasper Ridge Biological Preserve. Jasper Ridge is a 481-hectare (1,189-acre) preserve containing serpentine grasslands, chaparral hillsides, oak woodlands, freshwater wetlands, and mixed evergreen forests. The preserve has been designated a biological field station as extensive research has been conducted at the Preserve for over 100 years (Jasper Ridge Biological Preserve 1998).

The lower portion of the watershed is highly urbanized and is covered with impervious surfaces including parking lots, roads, commercial and residential buildings, driveways, and sidewalks. Stanford University, Stanford Golf Course, and Stanford Shopping Center border the Creek in Palo Alto.

METHODS

Overview

Stormwater samples were taken from 14 outfalls, 7 in the upper watershed and 7 in the lower watershed, during 3 separate storm events. Samples were collected during storm events that occurred in April 1999, November 1999, and January 2000. Samples were analyzed for diazinon, chlorpyrifos, nitrate, nitrite, orthophosphate, and ammonia.

Statistical analyses were performed to determine if there is a significant difference between pollutant contributions originating from the urban (lower) versus rural (upper) watershed and to determine if a significant difference exists between sites and the reference site. Correlation analysis was performed to determine if a relationship exists between the mean pollutant concentration originating from each outfall and the percent imperviousness of each corresponding catchment.

Sampling Sites

Fourteen study sites (outfalls) were chosen that represent the high and low impervious cover areas within the watershed, 7 in the upper watershed (low impervious cover) and 7 in the lower (high impervious cover). For the purpose of this thesis, the "upper" watershed refers to the portion of the watershed upstream of Junipero Serra Boulevard and the "lower" watershed is downstream of Junipero Serra Boulevard. Table 2 lists the location of sites including the nearest geographic reference, City, County, and on which side of the stream the outfall can be found. Figure 3 shows the location of each study site in the watershed and the division between the upper and lower watershed.

Sampling needed to occur at outfalls and selection of sampling sites was dependent on accessibility and location of the outfalls. First, sites had to be easily accessible, without risking the safety of the personnel collecting the samples. Second, outfalls had to be located on public property or on private property with the owner's permission or a permit. For example, a permit was obtained from Stanford Management Company to access sites 9, 10, 11,12, and 14. These were the only factors that limited the selection of sampling sites. To identify outfall locations, a creek walk was conducted from the mouth of San Francisquito Creek to Searsville Dam to locate all outfalls discharging into the Creek. One outfall chosen for analysis (Site 13) discharges into the tributary Bear Creek just upstream of the confluence of Bear and San Francisquito Creeks. Although not directly in San Francisquito Creek, this outfall was chosen due to the limited number of outfalls located in the upper watershed. In the rural upper watershed, most runoff enters the creek via overland flow and sampling this type of input was beyond the scope of this study. Outfalls that were not accessible from land due to steep slopes were not considered. All other outfalls and surrounding land uses were visually surveyed from the stream bank. The selected 14 outfalls were assigned numbers (starting with 1 at the further most downstream outfall) and marked with survey tape. During the creek walk, the

Creek and outfalls were mapped with a Trimble Navigation Pathfinder Pro XL Global Positioning System (GPS) unit for reproducibility and easy relocation. The GPS unit uses satellites to calculate and record the latitude and longitude of a feature with accuracy to within one meter.

Site 14 is the control or reference site for this study. Site 14, which is located in Jasper Ridge Biological Preserve, receives the fewest impacts and is not open to the public. The catchment area for Site 14 is relatively undisturbed and contains virtually no impervious area.

Outfall Number[1]	Latitude (NAD 27)	Longitude (NAD 27)	Geographic Reference	Stream Bank[2]	City	County
1	37.454287	122.131661	Across from 1835 Woodland Ave.	Left	East Palo Alto	San Mateo
2	37.454484	122.135281	Adjacent to Woodland Ave., just downstream of Newell Ave. bridge.	Left	East Palo Alto	San Mateo
3	37.453586	122.157156	At intersection of Palo Alto Ave. and Everett.	Right	Palo Alto	Santa Clara
4	37.447037	122.168064	At intersection of Palo Alto Ave. and Alma Ave.	Right	Palo Alto	Santa Clara
5	37.446154	122.171241	Behind Stanford Shopping Mall, upstream of El Camino Real bridge.	Right	Palo Alto	Santa Clara
6	37.430108	122.188858	Behind Oak Creek Apartments on Sand Hill Rd.	Right	Palo Alto	Santa Clara
7	37.428933	122.188937	Immediately downstream of Sand Hill Rd. bridge and Stanford Golf Course.	Left	Menlo Park	San Mateo
8	37.412602	122.193048	Webb Ranch Fruit stand.	Right	Stanford land	San Mateo
9	37.411871	122.197672	Portola Valley Training Center.	Left	Stanford land	San Mateo
10	37.411052	122.198320	Portola Valley Training Center, under Interstate 280 overpass.	Left	Stanford land	San Mateo
11	37.407234	122.211824	Boething Tree Farm.	Left	Stanford land	San Mateo
12	37.407140	122.212490	Boething Tree Farm.	Left	Stanford land	San Mateo
13	37.411417	122.239818	At intersection of Sand Hill Rd. and Whiskey Hill Rd. (drains into Bear Creek).	Left	Portola Valley	San Mateo
14	37.407332	122.238138	Jasper Ridge Biological Preserve, approximately 100 yards downstream of Searsville Dam.	Left	Stanford land	San Mateo

Table 2: Locations of outfalls (sites)

[1]Sites 1-7 are urban; Sites 8-14 are rural
[2]Bank side determined while facing downstream.

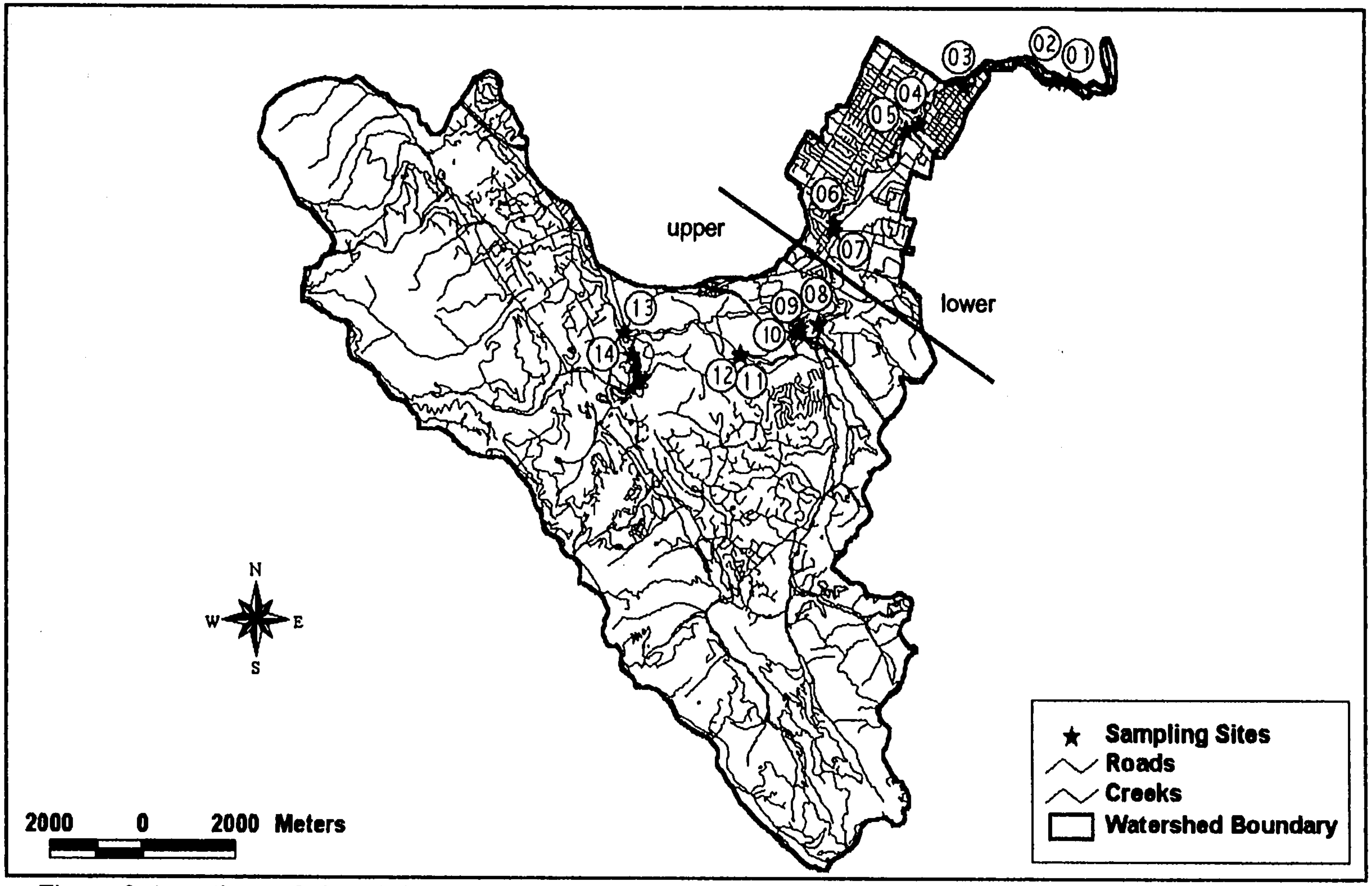


Figure 3: Locations of sites 1 through 14
(Produced by Jill Bernhard, Technical Specialist, Coyote Creek Riparian Station)

Land Use Characteristics

Catchment area. The area of each catchment[1] draining to each selected outfall was estimated using multiple methods (see Table 3 for areas of each catchment). Catchment areas of the sites located in the upper watershed, where there is steep terrain and varying topography, were calculated using a Geographic Information System (GIS) watershed model. This GIS model, called IDRISI™, uses a Digital Elevation Model[2] (DEM) to estimate the drainage pattern of a particular latitude and longitude within the watershed (Eastman 1995). The GIS results were compared against United Stated Geological Survey topographic maps in the field and were adjusted as needed. Catchment boundaries were delineated, as disccused in Gordon, McMahon, Finlayson (1992), using the contour lines on a United States Geological Survey, Palo Alto Quadrangle topographic map.

Catchment areas for sites located in the urbanized lower watershed were determined using storm drain maps. The GIS model was not utilized at these sites because natural drainage patterns based on topography are different than the drainage patterns that are now present with the storm drain system. Once the drainage boundary was determined, it was converted into a GIS layer to

[1] A catchment is defined as "the area above a specific point on a stream from which water drains toward the stream" (Gordon, McMahon, Finlayson 1992).

[2] The definition of a Digital Elevation Model as stated in the User's Guide (Eastman 1995) is as follows: "Digital Elevation Models – abbreviated DEM – is a term used to refer to an image which stores data that can be envisioned as heights on a surface. Although the grid structure breaks up the surface into cells of uniform character, the data are considered to come from an underlying continuous surface. The United States Geological Survey distributes a standard format DEM for much of the United States."

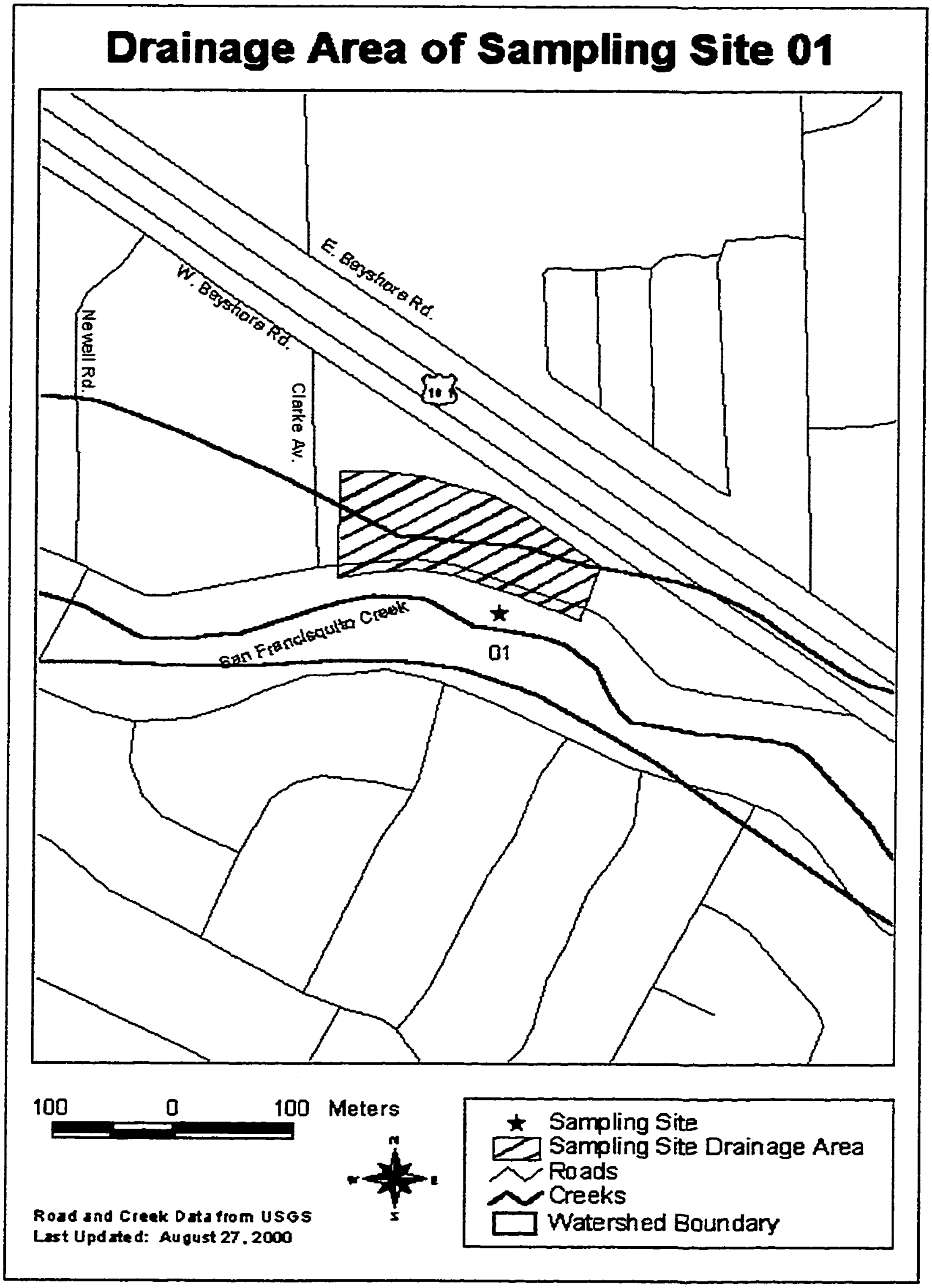
determine the area of the polygon. Figures 4 though 17 display the individual catchments for Sites 1 through 14.

Land use. The land uses located in each catchment and their respective areas were determined using a GIS layer of 1990 Association of Bay Area Governments (ABAG) land use data. The ABAG data has accuracy and spatial resolution suitable for identifying land use distribution and estimating the amount of impervious surface coverage within a catchment (Santa Clara Basin Watershed Management Initiative 2000). The ABAG land use categories each have a land use code associated with them. The land use data layer was overlain with the catchment area polygons to calculate the area of each land use within a catchment. Land uses were ground-truthed to verify accuracy and to take into account any changes in land uses in the past decade. This was done by visually surveying the catchments and noting any differences. In cases where land uses were not consistent with the ABAG data, the ground-truthed information was used by assigning it to one of the land use categories. For example, at sites 1 and 2, the ABAG data identified these catchments as containing Light Industrial uses. Upon further inspection at these sites, it was determined that there were no industrial land uses in these catchments, but rather residential.

Impervious surface coverage. The percent total impervious surface coverage, or imperviousness, was estimated for the different land uses for each catchment using multiple data sources. To estimate the percent imperviousness in each catchment, existing coefficients of imperviousness were used. Buchan, for the Santa Clara Basin Watershed Management Initiative (2000), has identified coefficients of imperviousness for 1995 ABAG land use data using work completed in two previous studies (Bredehorst 1981; Eisenberg, Olivieri, and Associates 1999). Some of the coefficients were truthed by the authors using a GIS. This was done by overlaying land uses on orthophotographs and digitizing impervious areas for up to 5 polygons (Santa Clara Basin Watershed Management Initiative 2000). Land use codes for the 1990 land use data were compared against the 1995 codes and were found to be consistent for the land uses found in the fourteen catchments. To determine the imperviousness of each catchment, the coefficient was multiplied by the acreage of each land use. For catchments that contain more than one land use type, the impervious areas were summed and divided by the total catchment area to obtain a total percentage of imperviousness in the catchment.

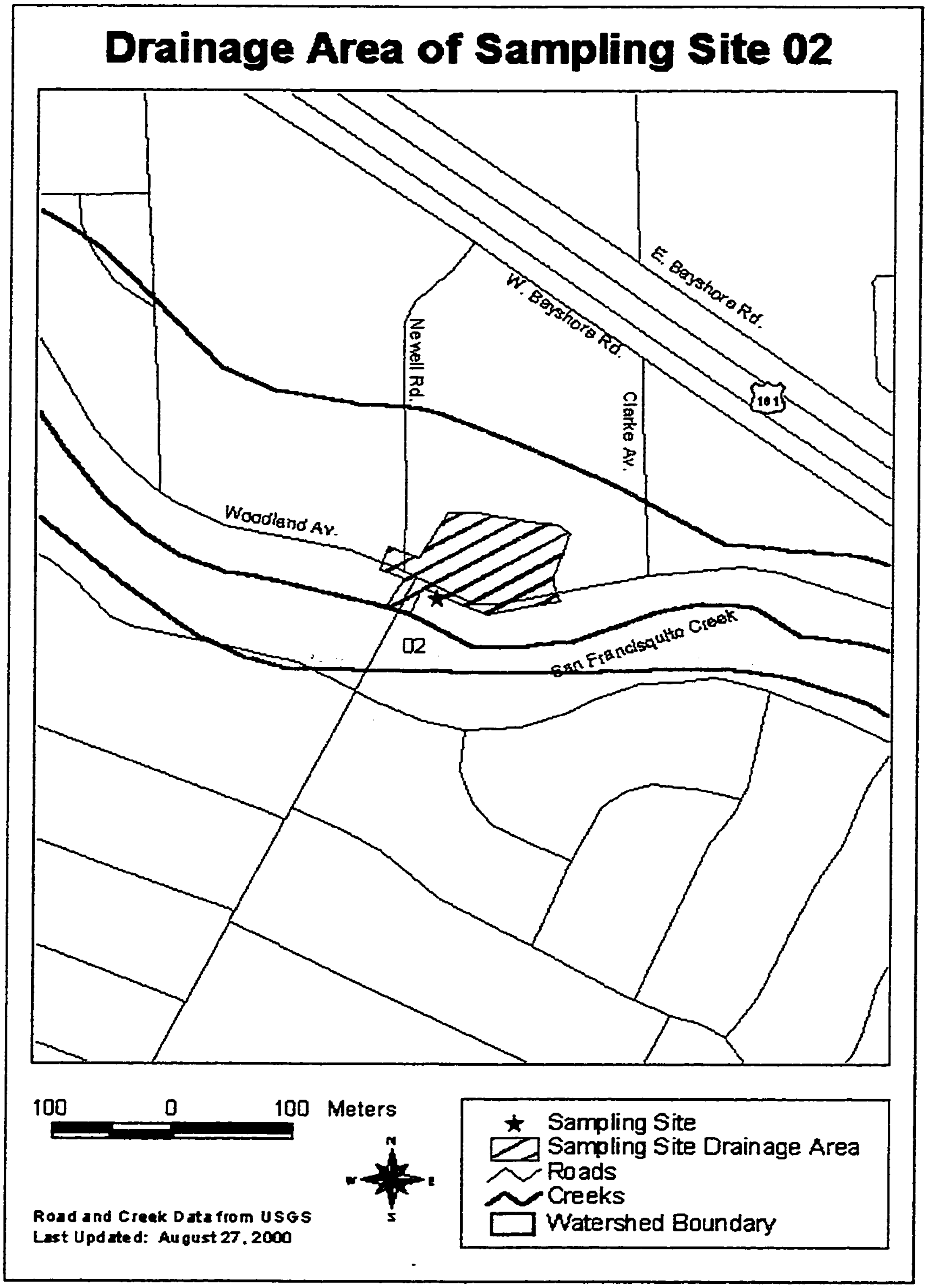
The characteristics of each study site including land use categories and codes, catchment area, coefficient of imperviousness, and percent imperviousness are shown in Table 3. Percent imperviousness for sites 1 through 14 is shown in Figure 18.

Figure 4: Drainage area for site 1, lower watershed (urban)



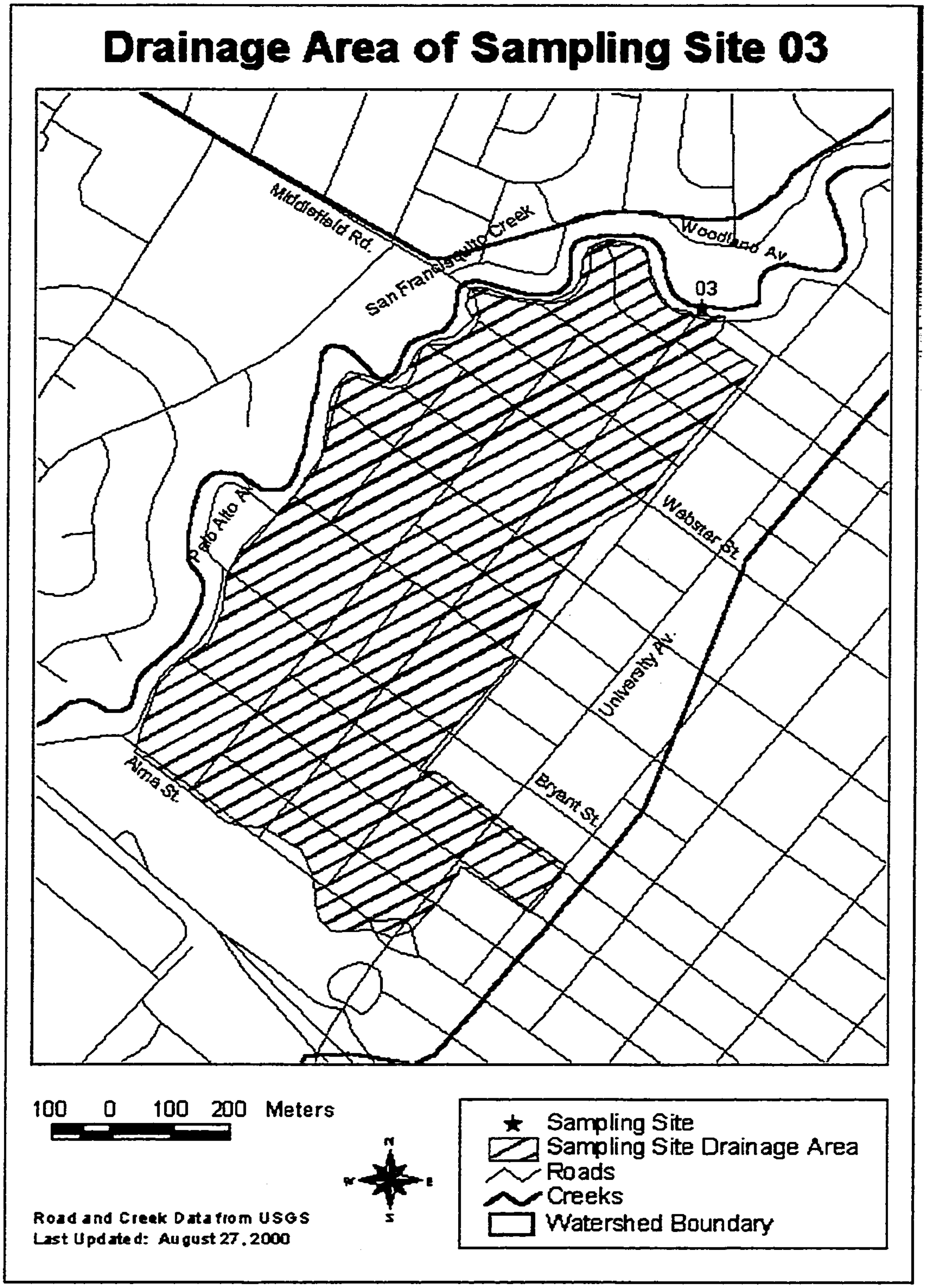
Map prepared by Jill Bernhard, Technical Specialist, Coyote Creek Riparian Station

Figure 5: Drainage area for site 2, lower watershed (urban)



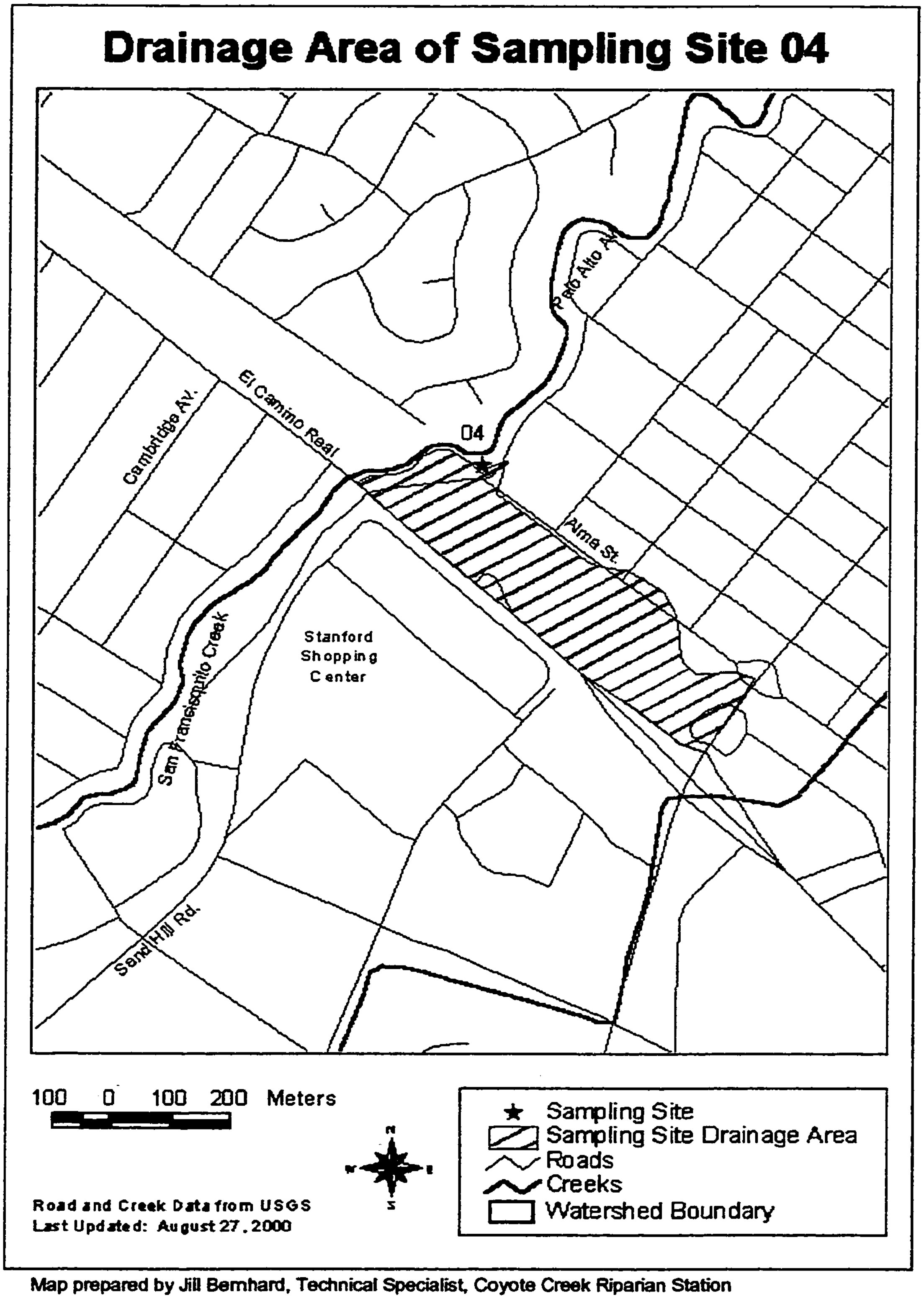
Map prepared by Jill Bernhard, Technical Specialist, Coyote Creek Riparian Station

Figure 6: Drainage area for site 3, lower watershed (urban)



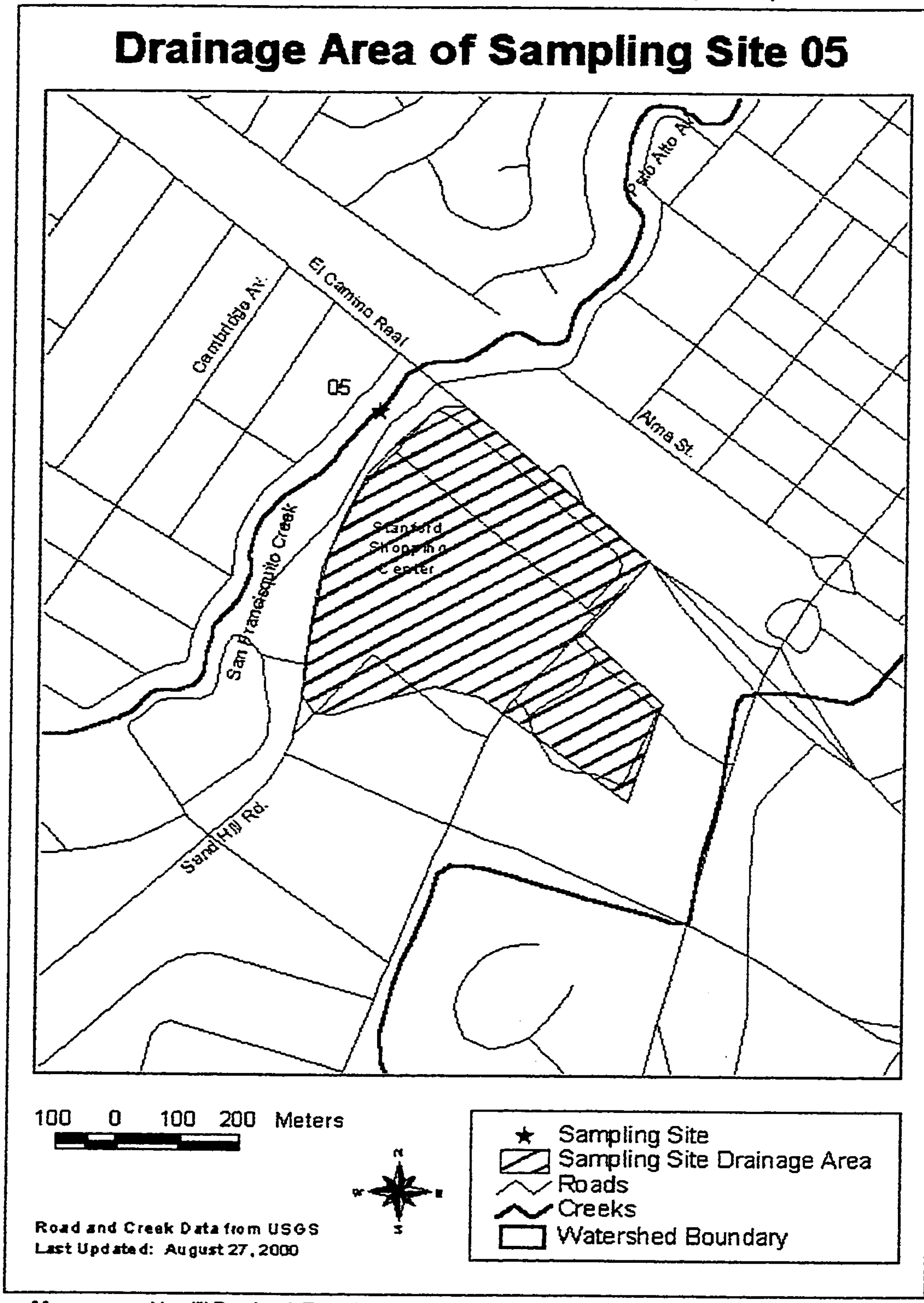
Map prepared by Jill Bernhard, Technical Specialist, Coyote Creek Riparian Station

Figure 7: Drainage area for site 4, lower watershed (urban)



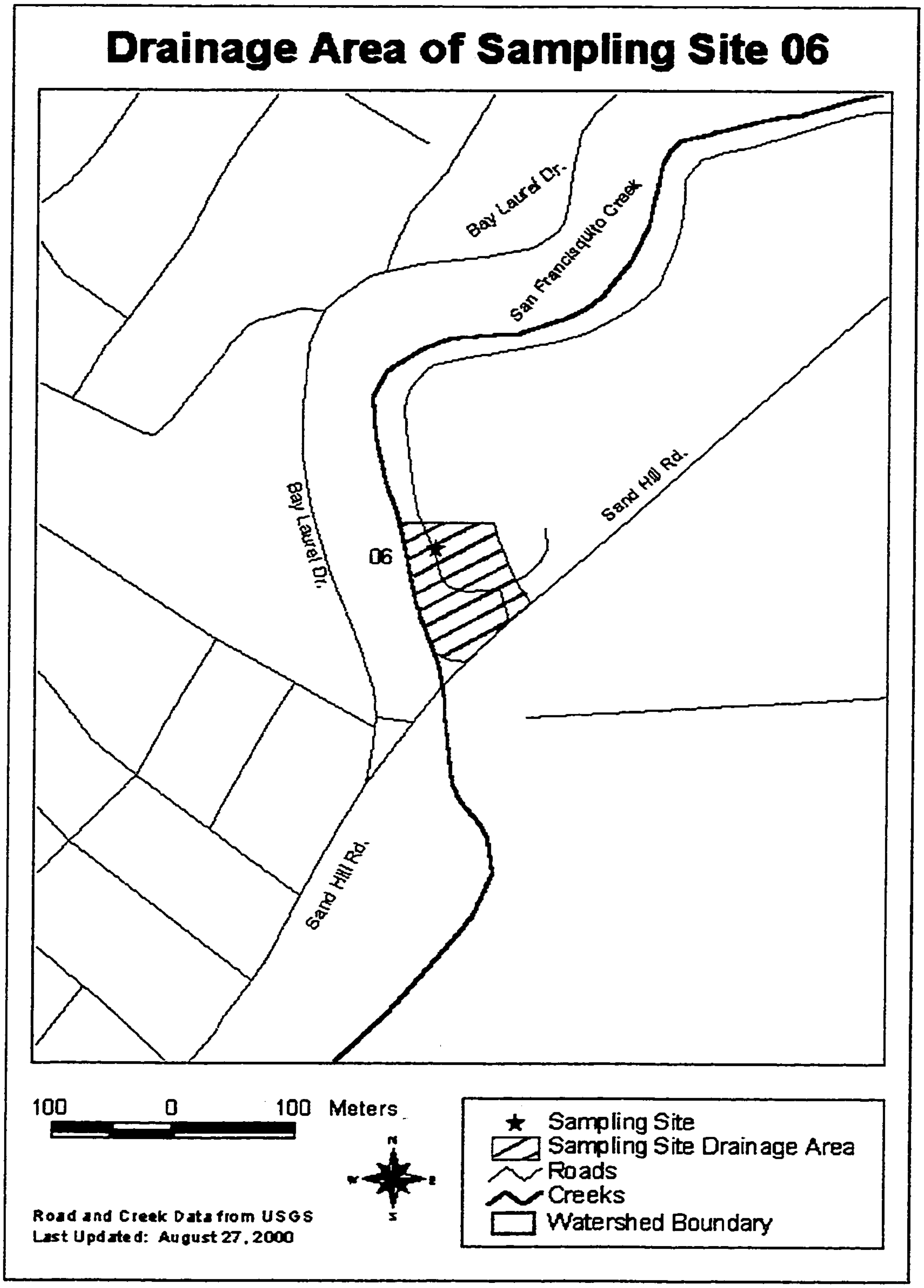
Map prepared by Jill Bernhard, Technical Specialist, Coyote Creek Riparian Station

Figure 8: Drainage area for site 5, lower watershed (urban)



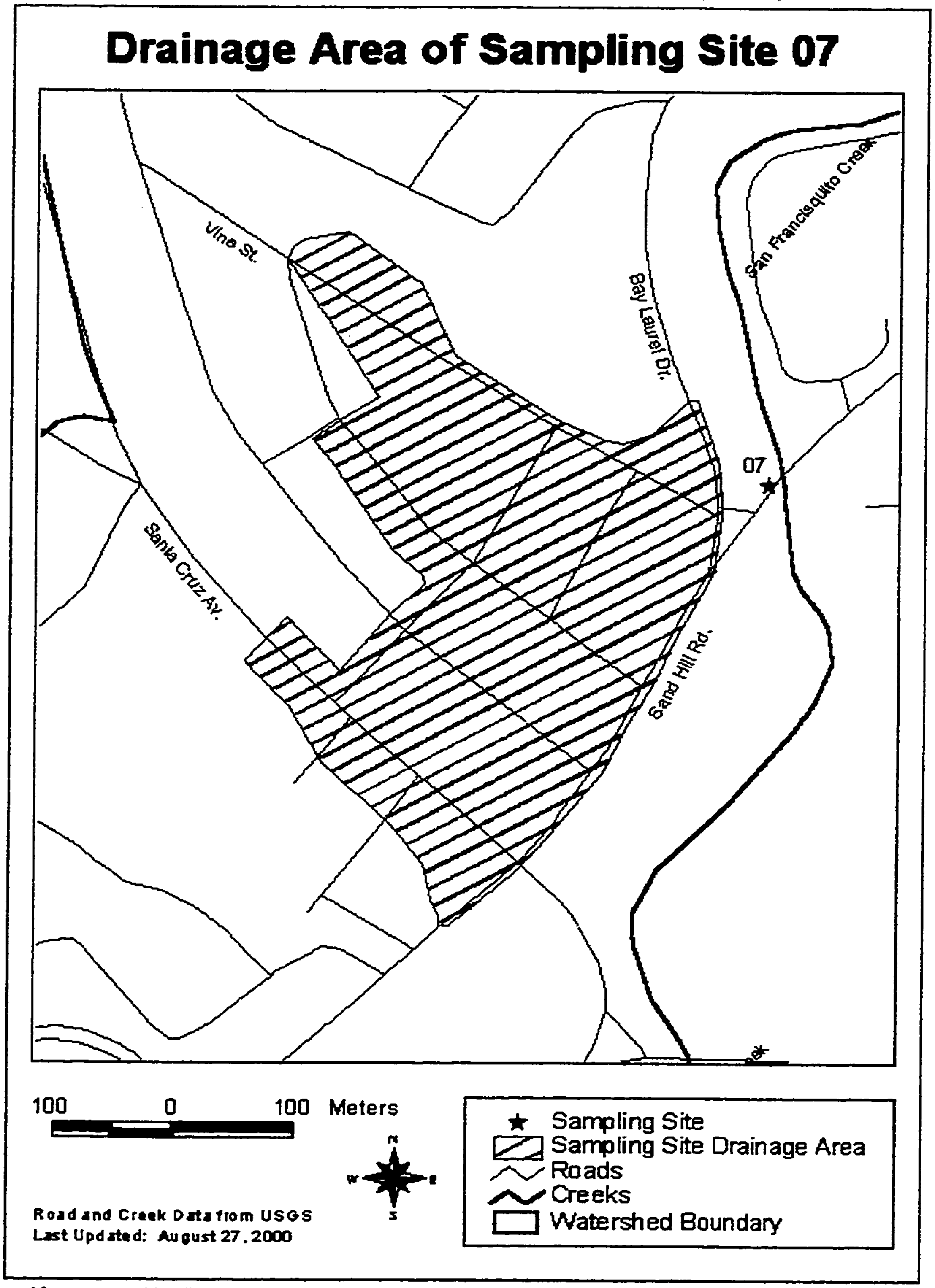
Map prepared by Jill Bernhard, Technical Specialist, Coyote Creek Riparian Station

Figure 9: Drainage area for site 6, lower watershed (urban)



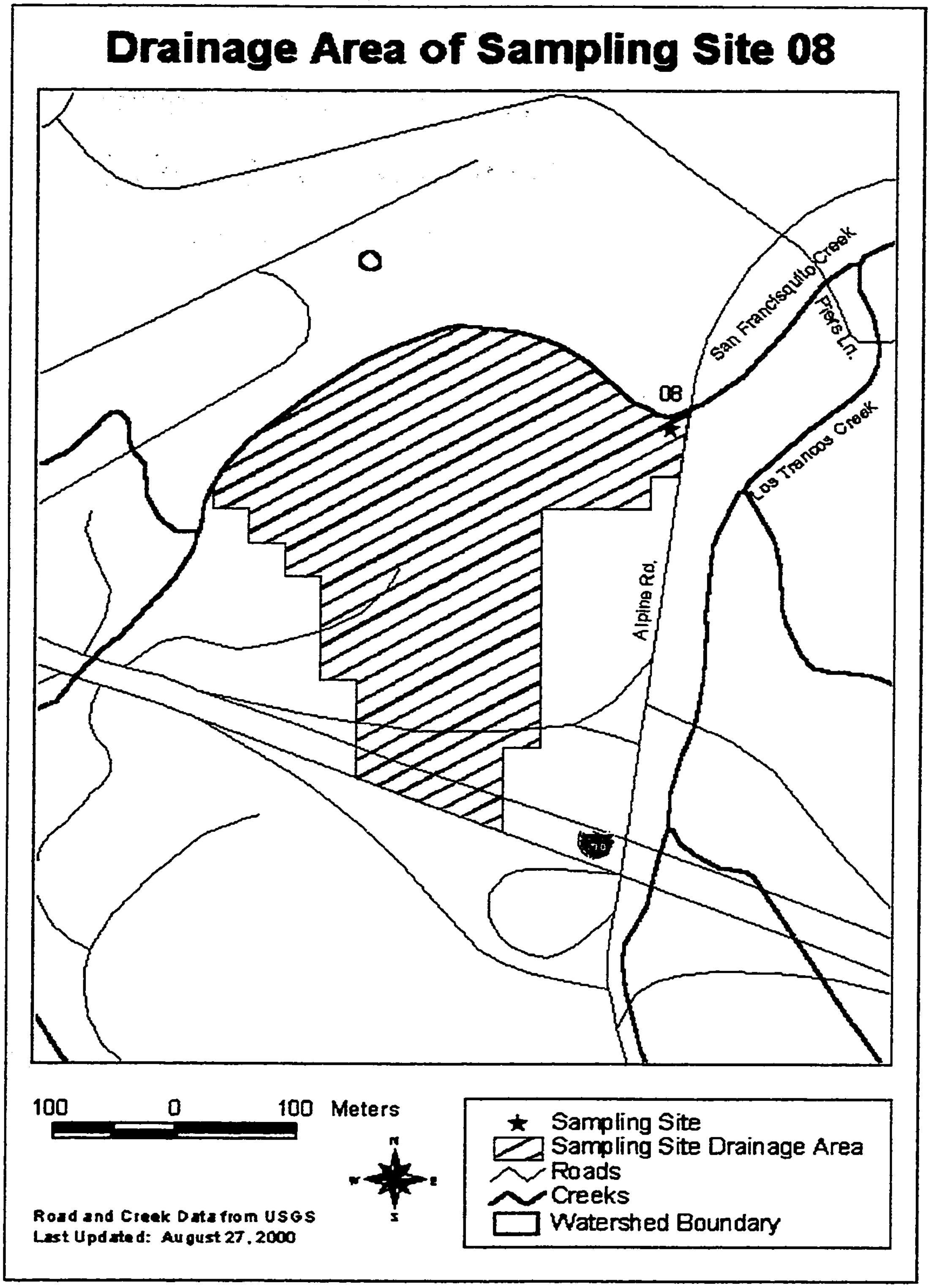
Map prepared by Jill Bernhard, Technical Specialist, Coyote Creek Riparian Station

Figure 10: Drainage area for site 7, lower watershed (urban)



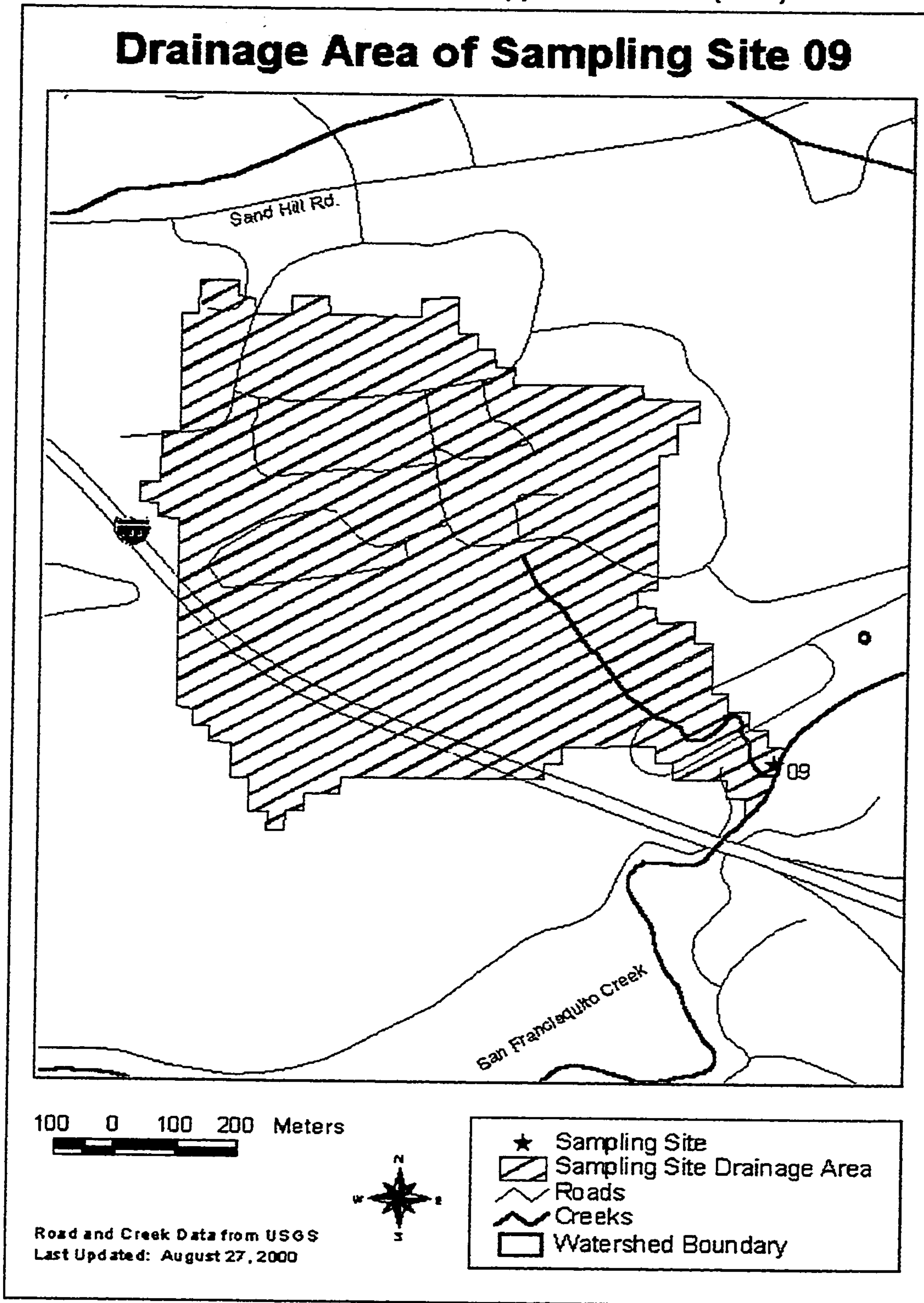
Map prepared by Jill Bernhard, Technical Specialist, Coyote Creek Riparian Station

Figure 11: Drainage area for site 8, upper watershed (rural)



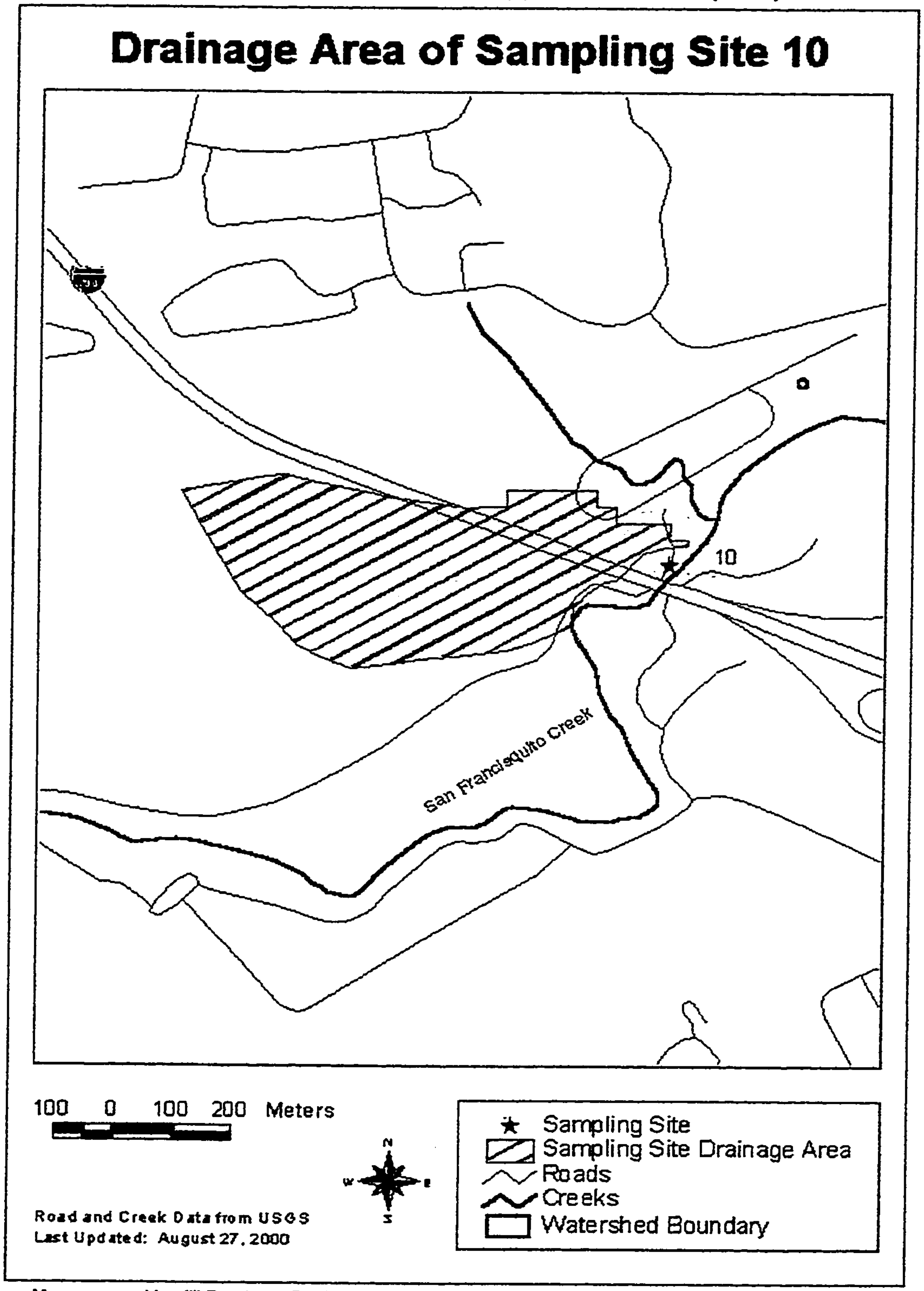
Map prepared by Jill Bernhard, Technical Specialist, Coyote Creek Riparian Station

Figure 12: Drainage area for site 9, upper watershed (rural)



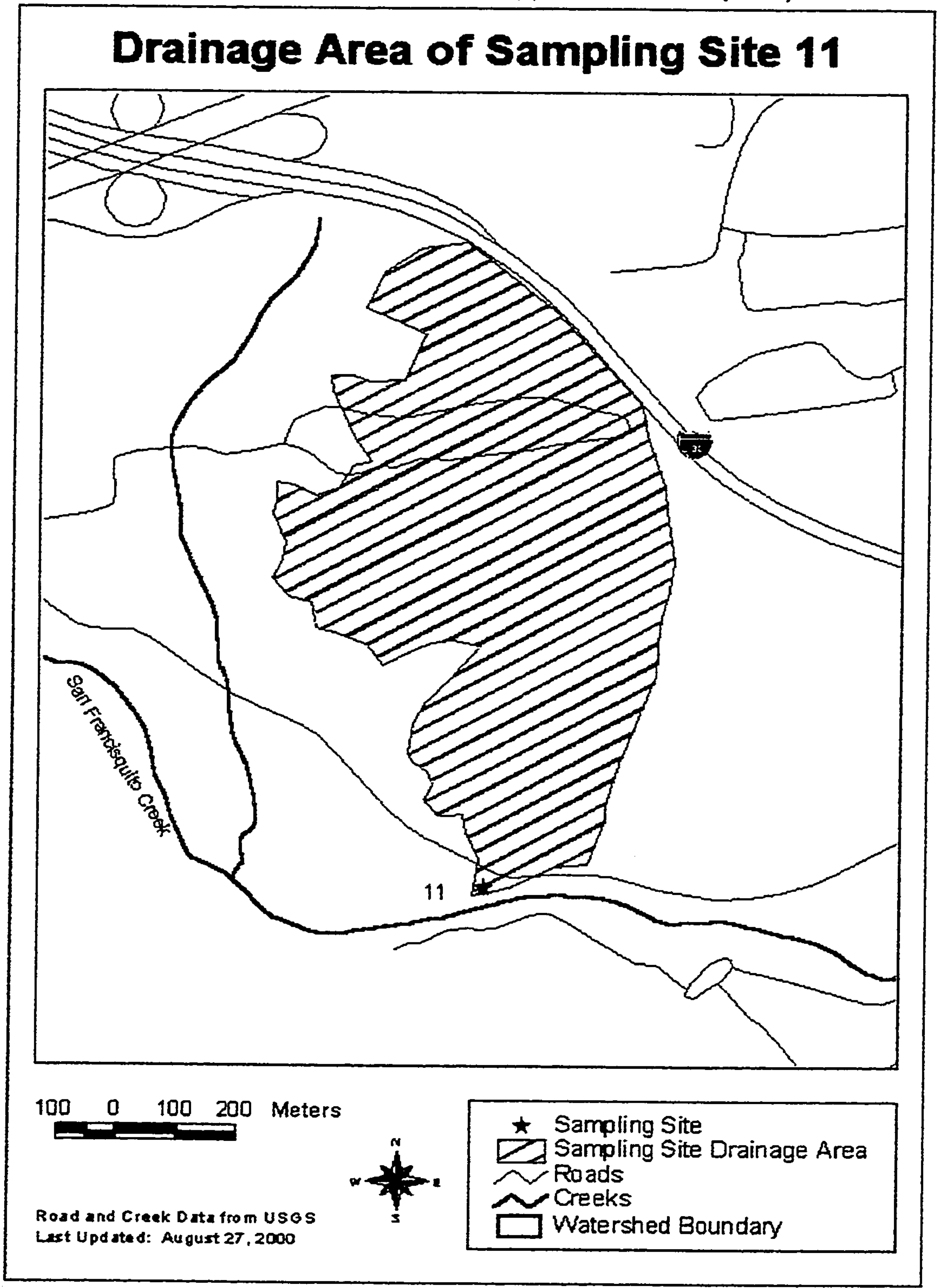
Map prepared by Jill Bernhard, Technical Specialist, Coyote Creek Riparian Station

Figure 13: Drainage area for site 10, upper watershed (rural)



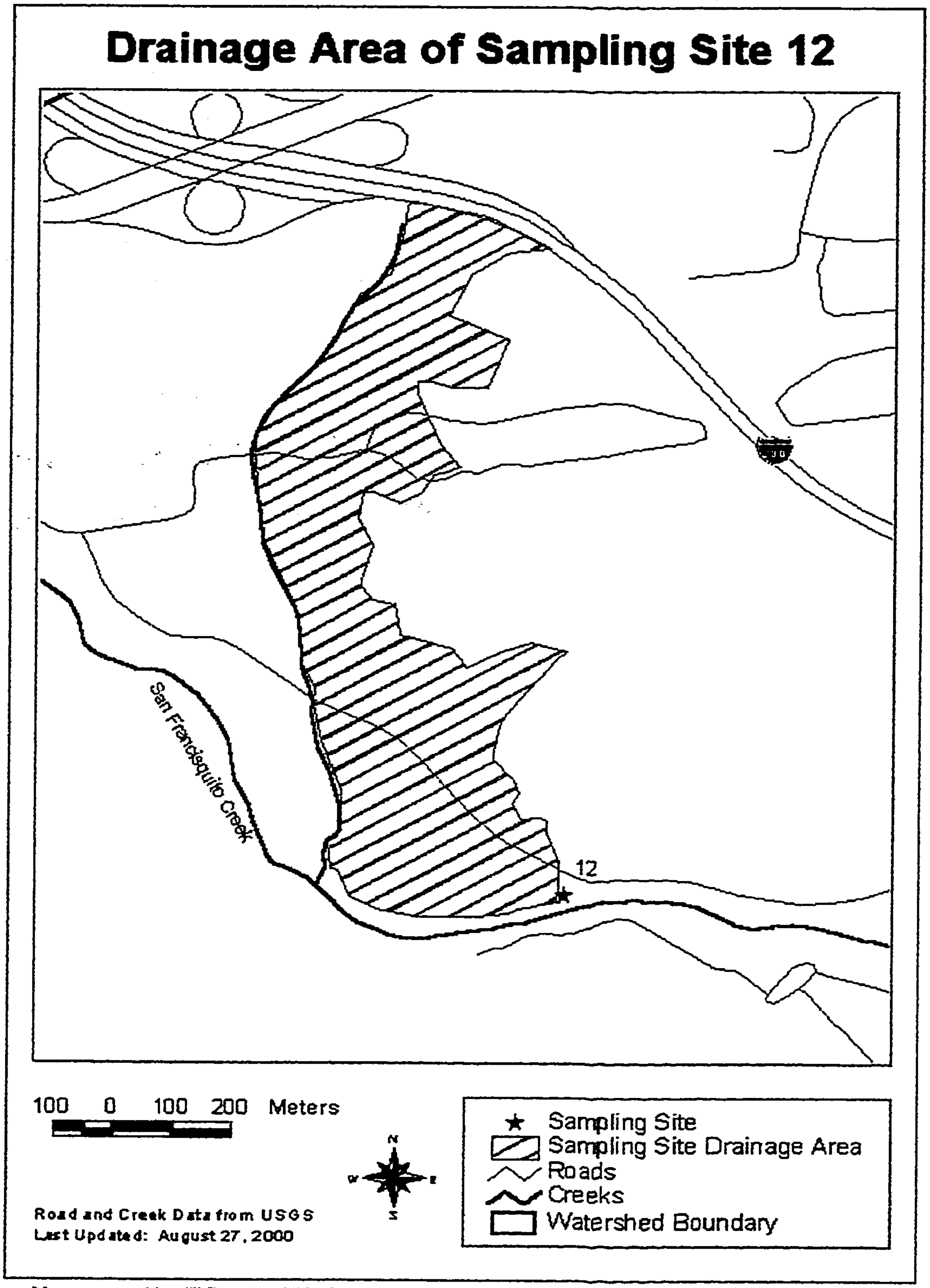
Map prepared by Jill Bernhard, Technical Specialist, Coyote Creek Riparian Station

Figure 14: Drainage area for site 11, upper watershed (rural)



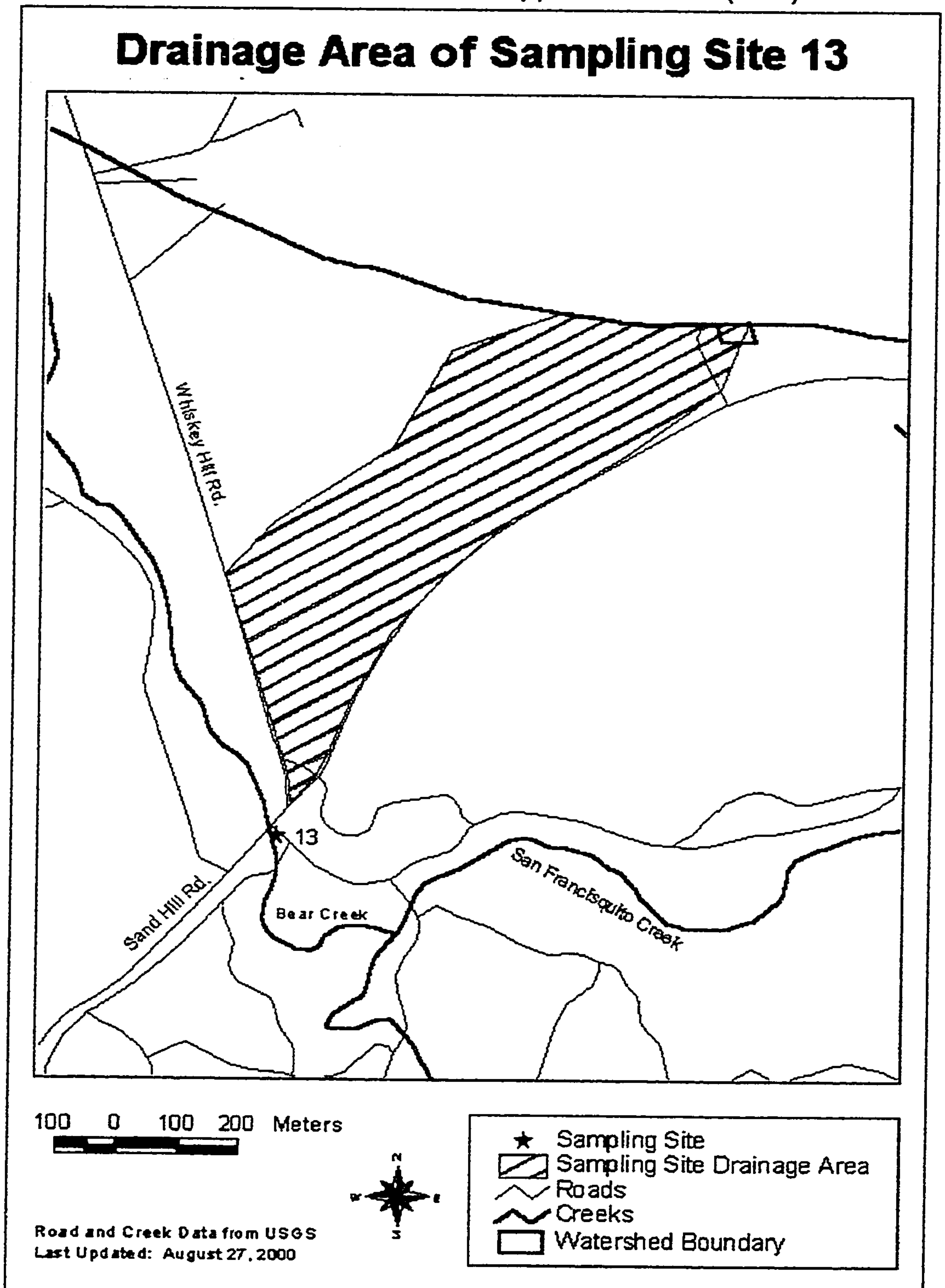
Map prepared by Jill Bernhard, Technical Specialist, Coyote Creek Riparian Station

Figure 15: Drainage area for site 12, upper watershed (rural)



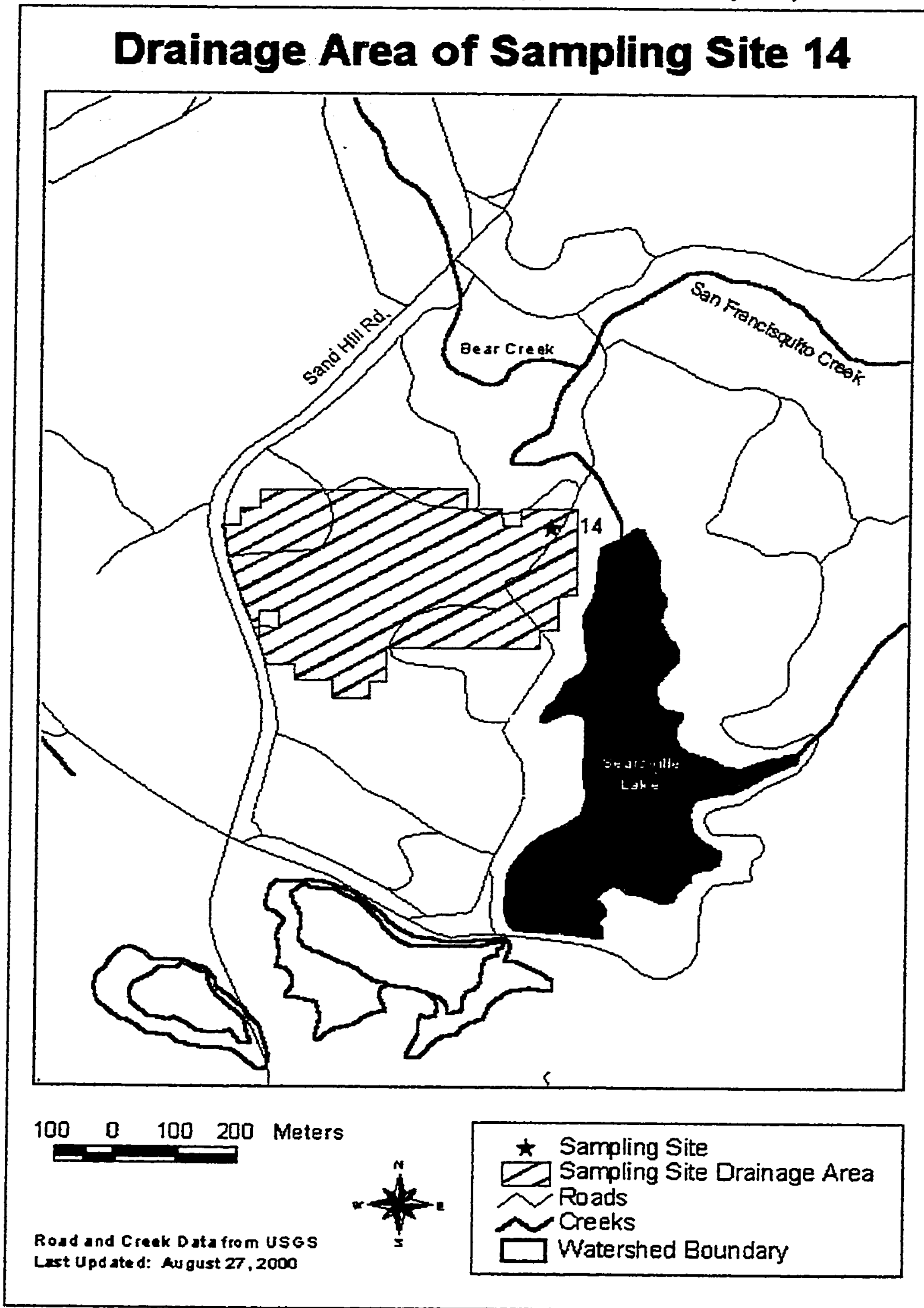
Map prepared by Jill Bernhard, Technical Specialist, Coyote Creek Riparian Station

Figure 16: Drainage area for site 13, upper watershed (rural)



Map prepared by Jill Bernhard, Technical Specialist, Coyote Creek Riparian Station

Figure 17: Drainage area for site 14, upper watershed (rural)



Map prepared by Jill Bernhard, Technical Specialist, Coyote Creek Riparian Station

SITE NO	AREA (square meters)	ACRES	LANDUSE CODE[1]	LEGEND[2]	COEFFICIENT	% IMPERVIOUSNESS[3]
1	1347.22	0.03	113	Nine and over DUs per hectare	0.81	
1	7020.61	0.16	141	Highways	0.9	
TOTAL		0.19				88.6
2	9711.41	0.22	113	Nine and over DUs per hectare	0.81	
TOTAL		0.22				81.0
3	469600.50	10.78	113	Nine and over DUs per hectare	0.81	
3	98108.27	2.25	16	Mixed urban and built up land	0.91	
TOTAL		13.03				82.7
4	58581.51	1.34	113	Nine and over DUs per hectare	0.81	
4	32878.43	0.75	16	Mixed urban and built up land	0.91	
4	276.82	0.01	175	Urban Vacant Land	0.01	
4	3393.29	0.08	12	Commercial and services	0.96	
4	14078.66	0.32	126	Other public institutions and facilities	0.82	
TOTAL		2.50				84.4
5	2887.11	0.07	113	Nine and over DUs per hectare	0.81	
5	210042.90	4.82	12	Commercial and services	0.96	
5	2835.57	0.07	126	Other public institutions and facilities	0.82	
5	5405.07	0.12	1232	Colleges and universities	0.47	
5	5052.06	0.12	1242	Community Hospitals	0.74	
5	2467.14	0.06	42	Evergreen Forest	0.01	
TOTAL		5.26				93.0
6	8630.01	0.20	113	Nine and over DUs per hectare	0.81	
TOTAL		0.20				81.0
7	79908.07	1.83	113	Nine and over DUs per hectare	0.81	
7	21893.43	0.50	1231	Elementary and Secondary schools	0.82	
7	13931.55	0.32	175	Urban Vacant Land	0.01	
TOTAL		2.65				71.6

Table 3: Catchment characteristics for sites 1-14

[1] 1990 Association of Bay Area Governments Land Use Codes
[2] DU = Dwelling Unit
[3] Santa Clara Basin Watershed Management Initiative (2000)

SITE NO	AREA (square meters)	ACRES	LANDUSE CODE[1]	LEGEND[2]	COEFFICIENT	% IMPERVIOUSNESS
8	28560.99	0.66	24	Farmsteads and other agriculture	0.02	
8	42506.60	0.98	2111	Irrigated	0.02	
8	1191.31	0.03	423	Evergreen Mix	0.01	
8	18060.59	0.41	31	Herbaceous Rangeland	0.01	
TOTAL		2.07				1.9
9	10135.59	0.23	31	Herbaceous Rangeland	0.01	
9	878.26	0.02	12	Commercial and services	0.96	
9	1490.57	0.03	31	Herbaceous Rangeland	0.01	
9	436379.12	10.02	127	Research Centers	0.96	
9	9717.81	0.22	31	Herbaceous Rangeland	0.01	
9	5435.35	0.12	141	Highways	0.9	
9	123295.25	2.83	31	Herbaceous Rangeland	0.01	
9	30170.98	0.69	24	Farmsteads and other agriculture	0.02	
9	9723.88	0.22	141	Highways	0.9	
9	14994.43	0.34	141	Highways	0.9	
TOTAL		14.74				69.9
10	59247.65	1.36	31	Herbaceous Rangeland	0.01	
10	30582.02	0.70	31	Herbaceous Rangeland	0.01	
10	34605.30	0.79	24	Farmsteads and other agriculture	0.02	
10	448.39	0.01	141	Highways	0.9	
10	20002.06	0.46	141	Highways	0.9	
10	29998.29	0.69	141	Highways	0.9	
10	4525.05	0.10	141	Highways	0.9	
TOTAL		4.12				28.5

Table 3 continued

[1] 1990 Association of Bay Area Governments Land Use Codes
[2] DU = Dwelling Unit
[3] Santa Clara Basin Watershed Management Initiative (2000)

SITE NO	AREA (square meters)	ACRES	LANDUSE CODE[1]	LEGEND[2]	COEFFICIENT	% IMPERVIOUSNESS[3]
11	7983.49	0.18	141	Highways	0.9	
11	362852.55	8.33	31	Herbaceous Rangeland	0.01	
11	7659.14	0.18	127	Research Centers	0.96	
11	6135.30	0.14	31	Herbaceous Rangeland	0.01	
11	27084.94	0.62	141	Highways	0.9	
11	20001.06	0.46	127	Research Centers	0.96	
11	10009.27	0.23	141	Highways	0.9	
11	4459.08	0.10	141	Highways	0.9	
TOTAL		10.24				16.8
12	17864.73	0.41	141	Highways	0.9	
12	272232.79	6.25	31	Herbaceous Rangeland	0.01	
12	8745.85	0.20	31	Herbaceous Rangeland	0.01	
12	21087.03	0.48	762	Transitional areas: other	0.02	
TOTAL		7.34				6.0
13	241326.13	5.54	31	Herbaceous Rangeland	0.01	
13	9741.98	0.22	0	Unclassified		
TOTAL		5.76				1.0
14	80985.92	1.86	423	Evergreen Mix	0.01	
TOTAL		1.86				1.0

Table 3 continued

[1] 1990 Association of Bay Area Governments Land Use Codes
[2] DU = Dwelling Unit
[3] Santa Clara Basin Watershed Management Initiative (2000)

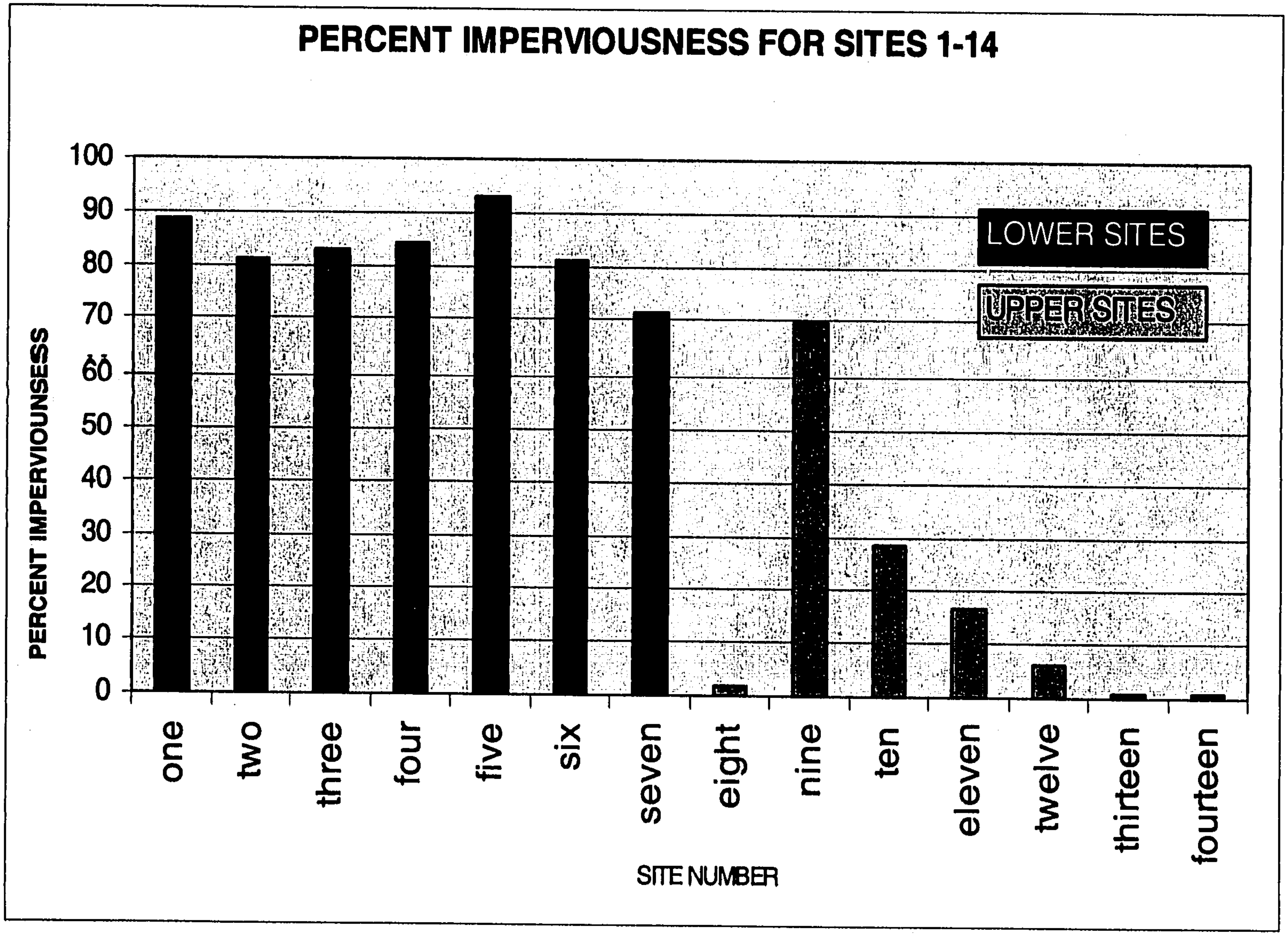


Figure 18: Percent impervious cover as estimated for each land use category for sites 1-14

Sample Collection

Water quality samples were collected from 14 separate stormdrain outfalls, 7 in the rural or upper watershed and 7 in the lower urbanized watershed at the start of 3 separate storm events. Events occurred at the beginning, middle, and end of the wet season to account for possible ranges in concentration.

The method of sample collection was modeled after those used in a study conducted by the City of Greensboro, North Carolina Environmental Services Department (City of Greensboro 1996) and a study by the Alameda Countywide Clean Water Program (1999). Grab samples were collected manually at the start of three separate storm events and stored at 4 degrees Celsius until analysis. Samples were collected in three separate amber glass containers with Teflon-lined caps. One container was for the laboratory tests of diazinon and chlorpyrifos, one was preserved with 1:1 hydrochloric acid for orthophosphate analysis, and the third was for the remaining nutrients. Volunteer assistants were used to collect the samples in the shortest time possible. Assistants were trained on collection techniques, safety, and the importance of collecting samples in a timely manner.

The first sample was collected at the end of the 1998-1999 wet season in April 1999. The second ánd third samples were collected at the beginning of the 1999-2000 wet season in November 1999 and in the middle of the wet season in January 2000. Storms were selected based on the length of time between storms and the time of year they occurred. A storm would only be considered if no precipitation had occurred during the 7 previous days.

Sampling occurred during events at various times of the year in order to capture storms representing the beginning, middle, and end of a season. An event at the start of the rainy season would typically have a longer period of time for pollutants to accumulate on surfaces and a high infiltration rate. Events in the middle and end of the rainy season would have less time for pollutant accumulation and less infiltration of precipitation as the ground would typically be saturated from previous storm events. Furthermore, certain pollutants may be used more or less frequently at varying times of the year depending on the land use. For example, homeowners may use pesticides or fertilizers at different times of the year than a commercial tree farm or horse training facility. Sampling throughout the rainy season takes into consideration possible differences in application practices.

Samples were collected from the first flush of each storm event in order to capture the maximum probable concentration of pollutants that have built-up since the last storm. The City of Greensboro (1996) recommends collecting the first flush sample within 30 minutes of initial runoff. The City of Sunnyvale collected a first flush sample within 60 minutes of initial runoff in an Industrial Stormwater Monitoring Pilot Project (Santa Clara Valley Urban Runoff Pollution Prevention Program 1998). All samples for this study were collected within the first 45 minutes of initial runoff.

Sample Analyses

A nutrient colorimeter (Hach/DR 890 brand) was used to measure concentrations of ammonia, nitrates, nitrites, and orthophosphates. This instrument has a wavelength accuracy of ±1nm, photometric accuracy of ±0.005 A, and photometric reproducibility of ±0.005 A. The precision for ammonia is ±5mg/L, for nitrates is ±0.2mg/L, for nitrites is ±0.004mg/L, and for phosphates is ±0.15mg/L (Hach Chemical Company 1997). A sample standard was prepared before each test run and all samples were analyzed according to the instrument manual directions, including collection, handling, and storage. Orthophosphate and ammonia were analyzed within 6 hours of collection. Nitrates and nitrites were analyzed within 24 hours.

Samples were analyzed for diazinon and chlorpyrifos within 48 hours of collection by Pacifica EcoRisk Laboratories in Martinez, California. Samples were analyzed using the enzyme-linked immunosorbent assay method, or ELISA.

Statistical Analyses

Statistical analyses were performed using Systat to determine if there is a significant difference between pollutant contributions originating from the urban (lower) versus rural (upper) watershed. Analyses were also performed to determine if a significant difference exists between sites and, if so, if that difference is significant between each site and the reference site. Correlation analysis was performed to determine if a relationship exists between the mean pollutant concentration originating from each outfall and the percent imperviousness of each corresponding catchment.

RESULTS

A total of 42 samples were collected during 3 storm events from April 1999 to January 2000 (Appendix A). Fourteen samples were collected for each storm event and analyzed for nitrate, nitrite, orthophosphate, ammonia, diazinon, and chlorpyrifos. The mean concentration of the three storms was calculated for all 14 sites.

Mean diazinon concentrations were highest in the lower more urbanized watershed, particularly at sites 2 through 5 (Figure 19), and ranged from 0.103 to 0.549 ug/l, versus a range of 0.040 ug/l to 0.184 ug/l for the upper watershed. Chlorpyrifos concentrations tended to be higher in the upper watershed, which consists of open space and agricultural land uses (Figure 20). Mean concentrations ranged from 0.063 to 0.345 ug/l in the upper watershed, versus a range of 0.064 ug/l to 0.177 ug/l in the lower watershed.

Mean concentrations for nitrate, nitrite, and orthophosphate were higher in the upper watershed than the lower watershed (Figures 21 through 23). The highest mean concentrations were found at sites 11 and 12 for all three nutrients. Mean ammonia concentrations varied throughout the entire watershed (Figure 24), although site number 11 had the highest concentration of any of the sites.

Figure 19: Mean diazinon concentration for sites 1 through 14

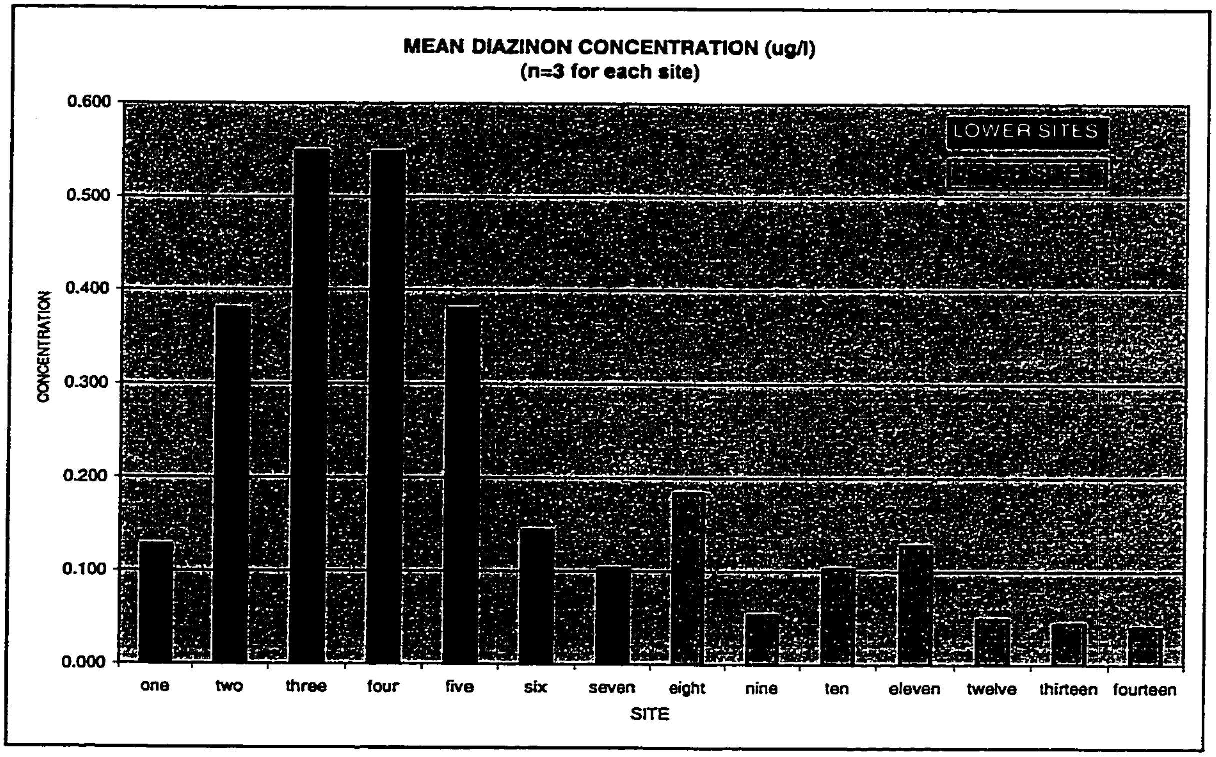


Figure 20: Mean chlorpyrifos concentration for sites 1 through 14

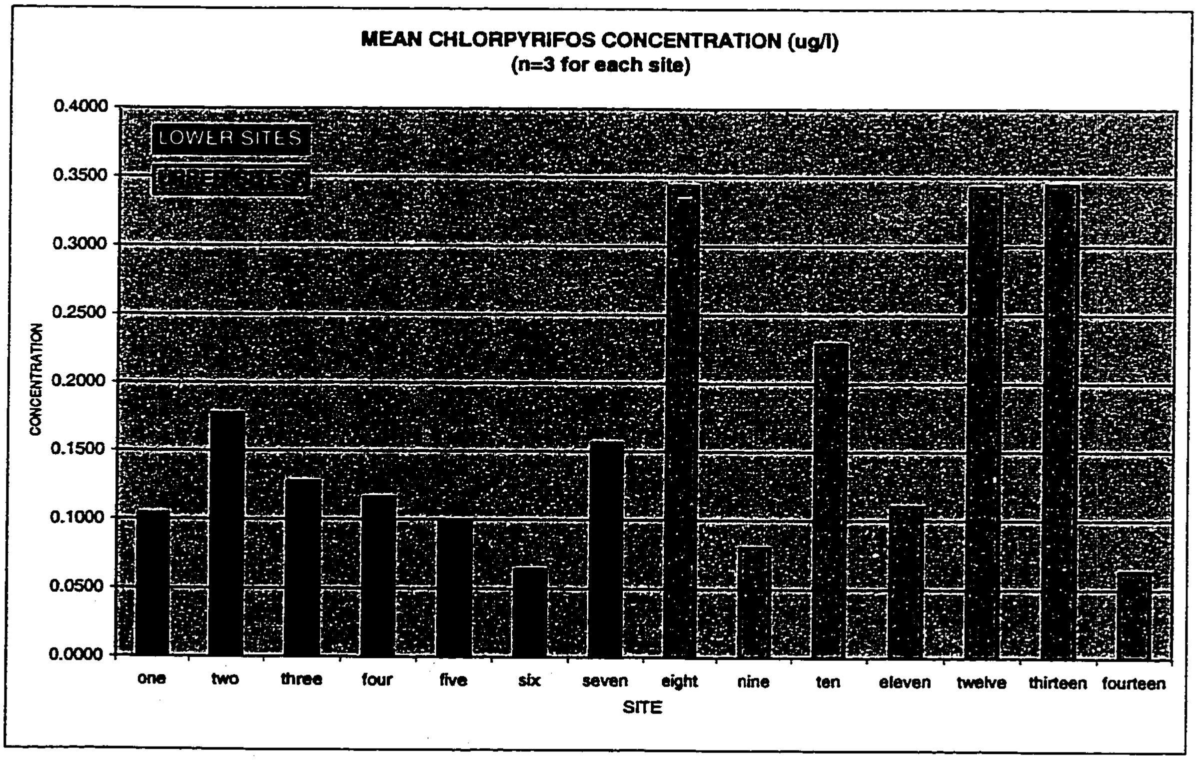


Figure 21: Mean nitrate concentration for sites 1 through 14

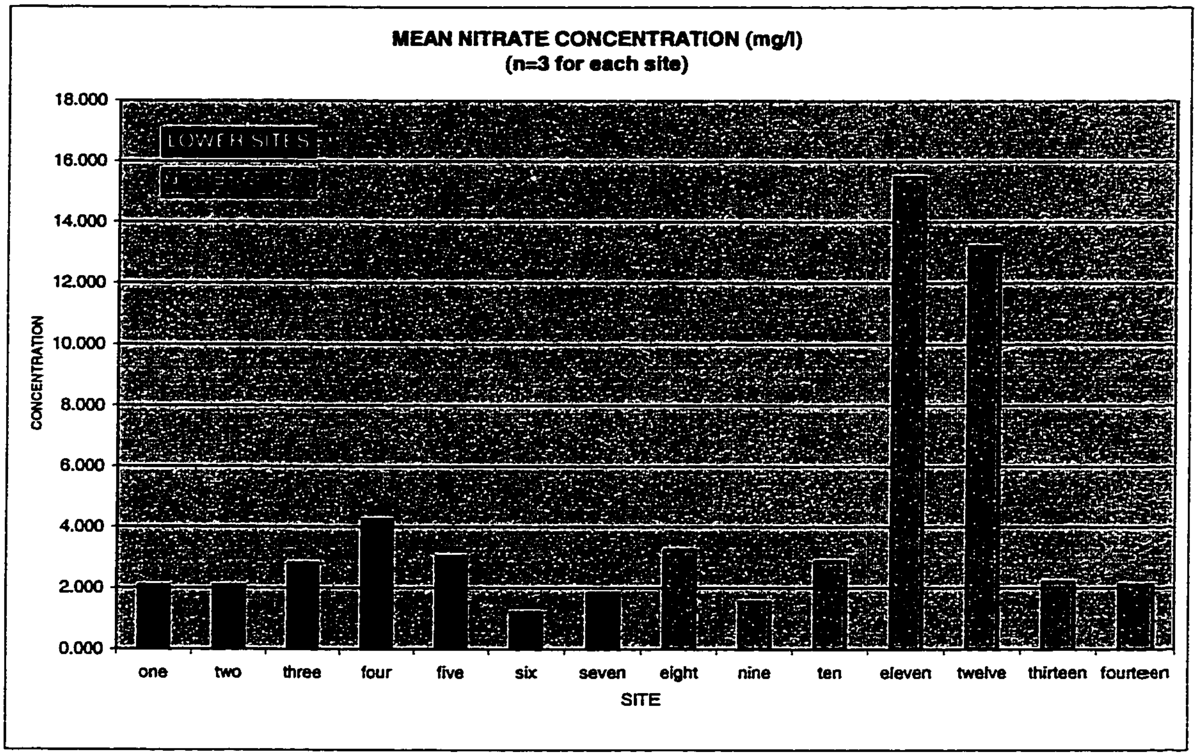


Figure 22: Mean nitrite concentration for sites 1 through 14

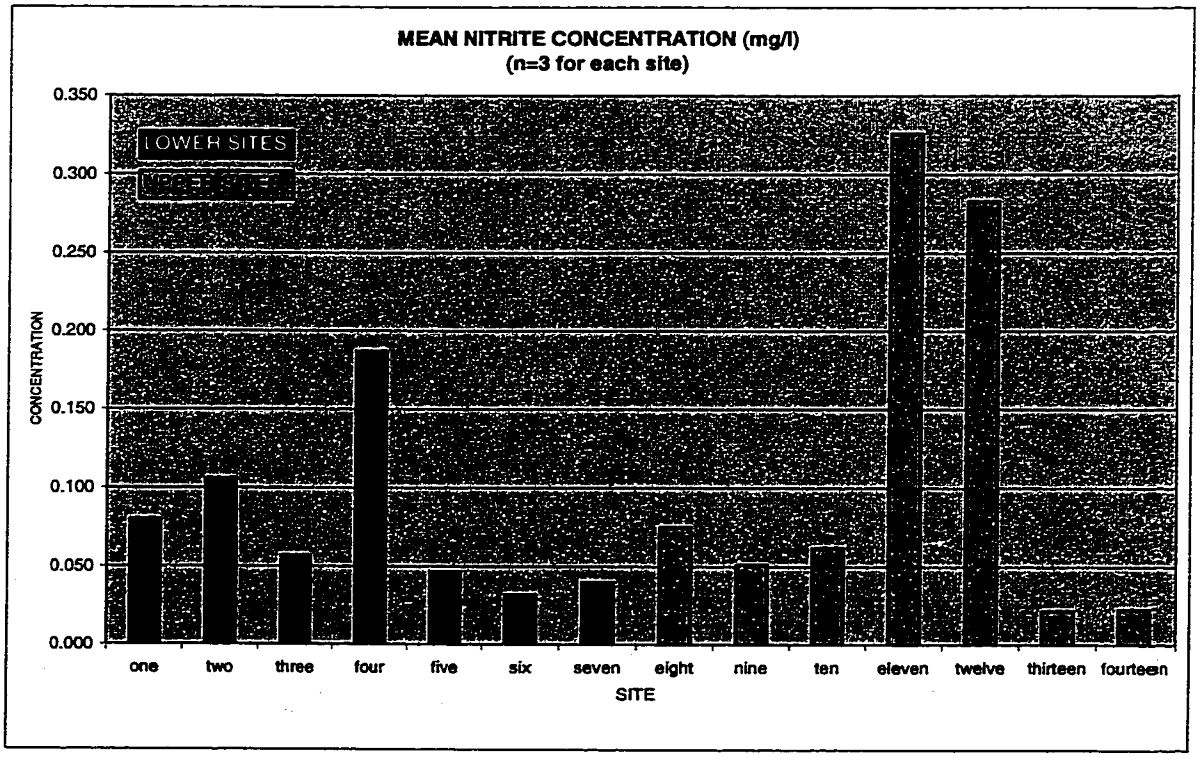


Figure 23: Mean orthophosphate concentration for sites 1 through 14

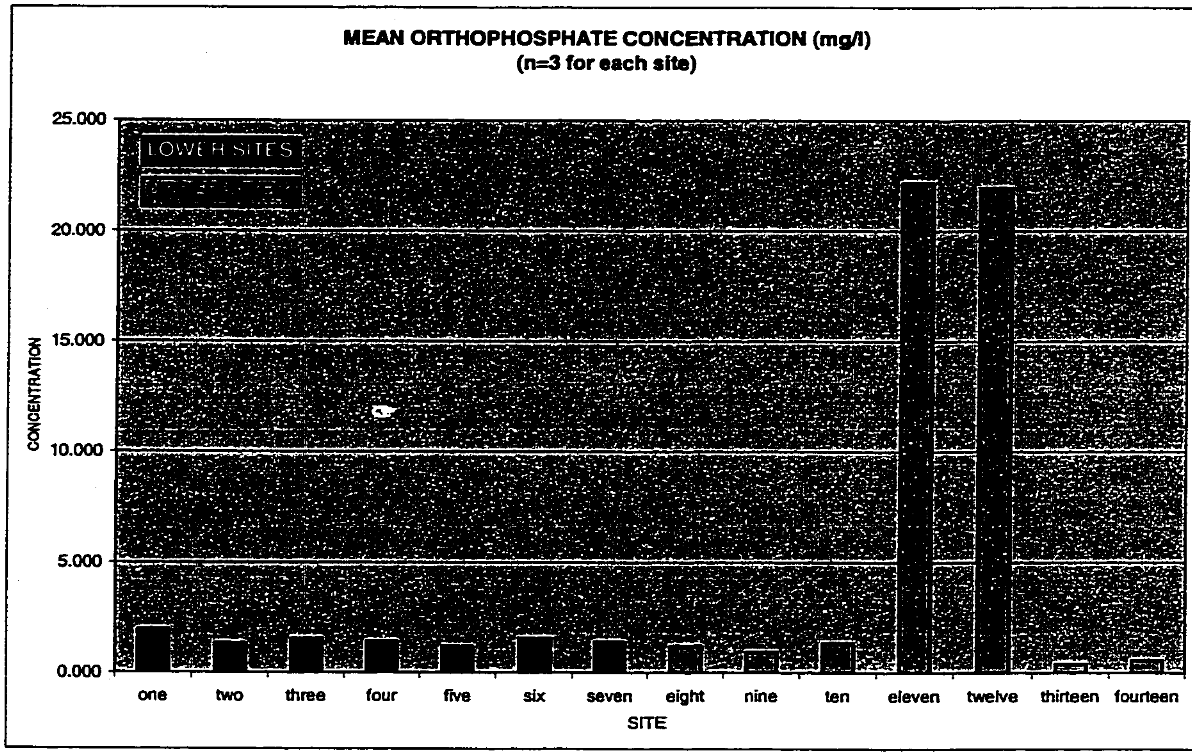
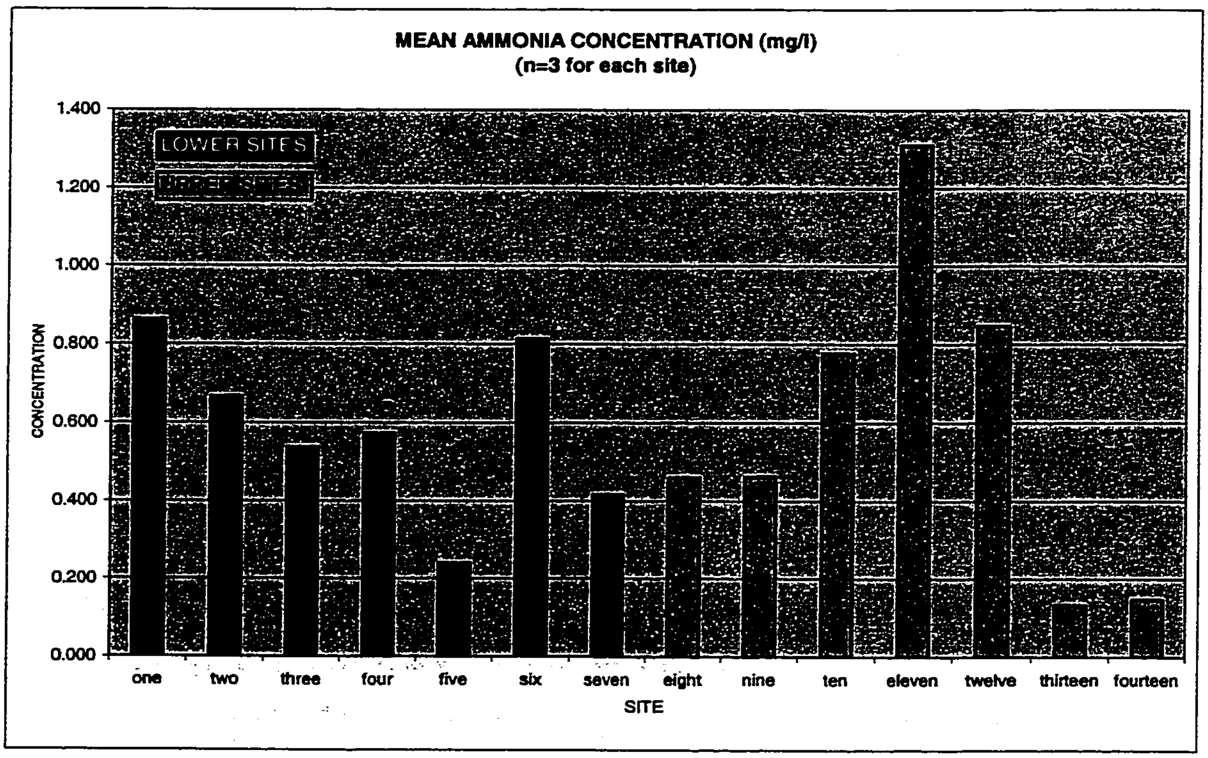


Figure 24: Mean ammonia concentration for sites 1 through 14



A Bartlett test for equal variances was done for each pollutant to determine if the data followed a normal distribution pattern. The null hypothesis (H_O:$\sigma_{upper\ sites}$=$\sigma_{lower\ sites}$) was rejected for four out of the six pollutant tests (Table 4), meaning the variance in the upper watershed was not equal to the variance in the lower watershed for the four pollutants. This is an indication that the data does not follow a normal distribution pattern and nonparametric statistics should be used (Zar 1996).

Table 4: Results of Bartlett test for equal variances

PARAMETER	alpha	p-value	Accept/ Reject H_o
Diazinon	0.05	0.007	Reject
Chlorpyrifos	0.05	0.008	Reject
Nitrate	0.05	0.0004	Reject
Nitrite	0.05	0.056	Accept
Orthophosphate	0.05	0.000000003	Reject
Ammonia	0.05	0.136	Accept

Diazinon was the only measured constituent for which the null hypothesis (H_O: $\mu_{upper\ sites} = \mu_{lower\ sites}$) was rejected for the Mann-Whitney U test (Table 5). This means there is a significant difference between pollutant concentrations in the upper watershed and the lower watershed. There was no significant difference in concentration between the upper and lower sites for the other pollutants tested.

Table 5: Results of Mann-Whitney U test (n=7)

PARAMETER	**alpha**	**p-value**	**Accept/ Reject H_o**
Diazinon	0.05	0.012	Reject
Chlorpyrifos	0.05	0.338	Accept
Nitrate	0.05	0.224	Accept
Nitrite	0.05	0.949	Accept
Orthophosphate	0.05	0.338	Accept
Ammonia	0.05	0.749	Accept

An Analysis of Variance (ANOVA) was performed on all parameters to compare the 14 sites to each other and to determine if a significant difference exists in pollutant concentration between the sites. The null hypothesis (H_O: $\mu_1=\mu_2=\ldots\mu_{14}$) was rejected for four out of the six tests meaning there is a significant difference between some of the sites (Table 6). The four pollutants that showed the significant differences between sites were diazinon, nitrate, nitrite, and orthophosphate. Neither chlorpyrifos nor ammonia showed a significant difference in pollutant concentration between sites.

Table 6: Results of Analysis of Variance (ANOVA)

PARAMETER	alpha	p-value	Accept/ Reject H_o
Diazinon	0.05	0.0185	Reject
Chlorpyrifos	0.05	0.7904	Accept
Nitrate	0.05	0.0012	Reject
Nitrite	0.05	0.0007	Reject
Orthophosphate	0.05	0.0001	Reject
Ammonia	0.05	0.1866	Accept

An *a posteriori* Dunnett's test was performed on the diazinon, nitrate, nitrite, and orthophosphate data to compare each of the first thirteen sites to a reference site (site 14). The results of the Dunnett's test on diazinon show that sites 3 and 4 were significantly higher than site 14. For nitrate, nitrite, and orthophosphate, sites 11 and 12 were significantly higher than site 14. Table 7 shows the results of the Dunnett's test.

Table 7: Results (p-values) of Dunnett's test with alpha=0.05

	Diazinon	**Nitrate**	**Nitrite**	**Orthophosphate**
SITES				
1&14	0.999	1.0000	0.9836	1.000
2&14	0.298	1.0000	0.8389	1.000
3&14	**0.037***	1.000	0.999	1.000
4&14	**0.033***	0.998	0.148	1.000
5&14	0.299	1.000	1.000	1.000
6&14	0.999	1.000	1.000	1.000
7&14	1.000	1.000	1.000	1.000
8&14	0.979	1.000	0.992	1.000
9&14	1.000	1.000	1.000	1.000
10&14	0.999	1.000	0.999	1.000
11&14	1.000	**0.002***	**0.001***	**0.001***
12&14	1.000	**0.014***	**0.005***	**0.001***
13&14	1.000	1.000	1.000	1.000

* significant p-value ($p<0.05$)

Water quality data was correlated against imperviousness to determine if a relationship exists between pollutant concentration and the percent of catchment covered with impervious surfaces (Table 8). Pearson's Product-Moment correlation analysis showed that a positive correlation (r= 0.602) exists between imperviousness and concentration for diazinon and a negative correlation (r= -0.633) exists for chlorpyrifos. Figure 25 shows that diazinon concentrations tend to be higher at the urban sites, while Figure 26 shows the opposite pattern for chlorpyrifos. No correlation was found between the four nutrients tested and imperviousness in this study.

Table 8: Results of Pearson's Product-Moment Correlation

PARAMETER	Alpha	p-value	Significant Correlation?
Diazinon	0.05	0.018	Yes
Chlorpyrifos	0.05	0.025	Yes
Nitrate	0.05	0.109	No
Nitrite	0.05	0.376	No
Orthophosphate	0.05	0.129	No
Ammonia	0.05	0.751	No

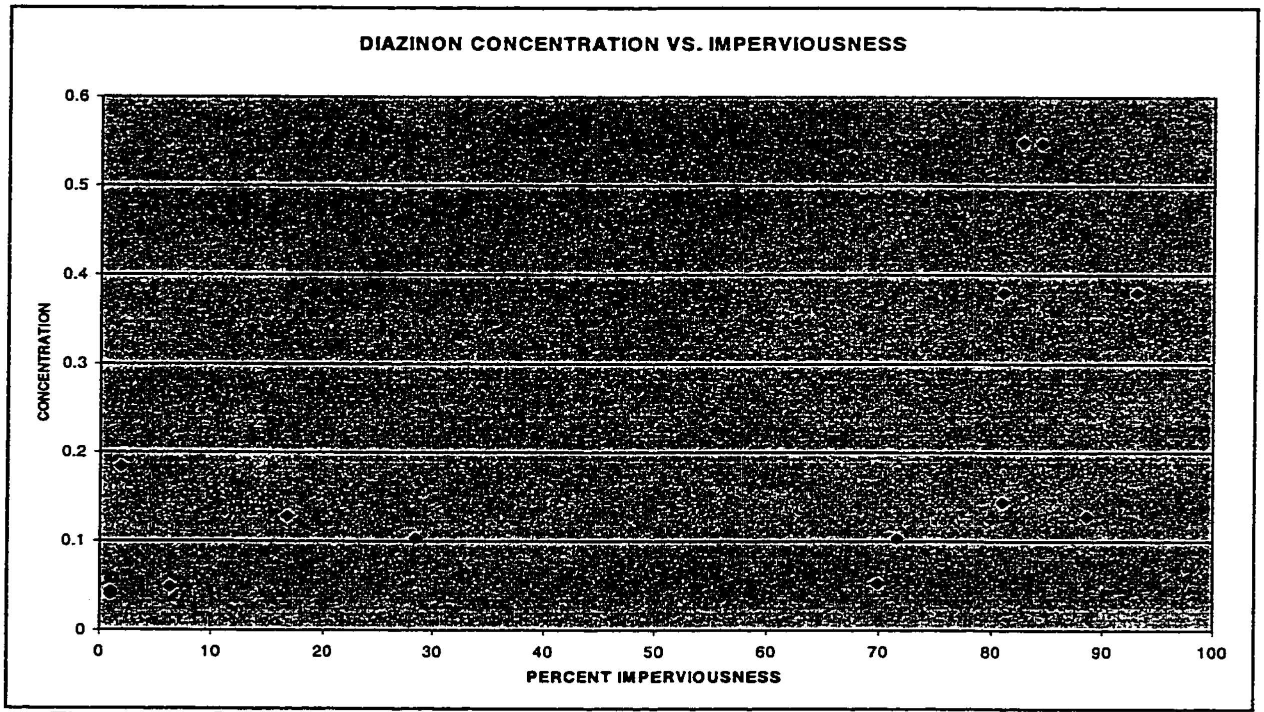


Figure 25: Scatterplot of the average diazinon concentration at the 14 sites versus percent impervious cover at those sites.

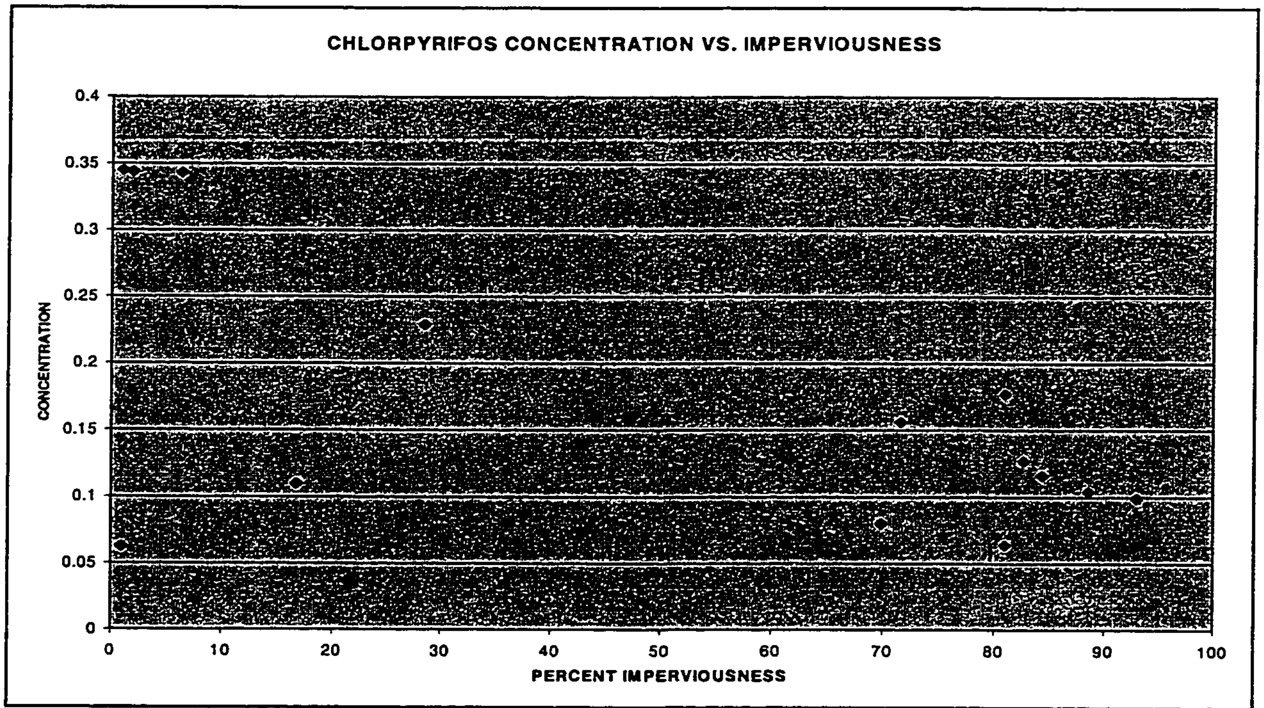


Figure 26: Scatterplot of the average chlorpyrifos concentration at the 14 sites verus percent impervious cover at those sites.

DISCUSSION AND RECOMMENDATIONS

The objectives of this study were to determine if a significant difference exists in nutrient and pesticide concentrations between urban and rural stormwater runoff, if mean concentrations were higher than those at a reference site, and if a relationship exists between pollutant concentration and percent imperviousness. This study confirmed that diazinon is a significant pollutant entering San Francisquito Creek. Chlorpyrifos and nutrients are also major pollutants. This work went further to show the general sources of these pollutants in the watershed.

Upper Watershed versus Lower Watershed

A significant difference was found between the upper and lower watershed for diazinon only. Concentrations of diazinon were higher in the lower, more urbanized watershed where residential and commercial land uses dominate. This is consistent with the literature that connects diazinon to toxicity in surface water in urban areas (Alameda Countywide Clean Water Program 1999; Cooper 1996; and Katznelson and Mumley 1997). The Alameda Countywide Clean Water Program (1999) reported that stormwater samples collected in Alameda County and throughout the San Francisco Bay Area were often toxic to *Ceriodaphnia dubia*. Toxicity identification evaluations linked toxicity to diazinon. Katznelson and Mumley (1997) reported that diazinon was detected during storm events in San Leandro Creek.

Comparison to Reference Site

Analysis conducted comparing each site to site 14, the reference site, showed that significant differences in concentration existed for diazinon, nitrate, nitrite, and orthophosphate for some sites. When comparing the concentrations of these four parameters to the reference site, significant differences were found. For diazinon, sites 3 and 4 were significantly higher than the reference site. These two sites are located in Palo Alto along Palo Alto Avenue. The primary land use for site 3 is high density residential (83 percent). The primary land uses for site 4 are high density residential (54 percent) and mixed urban (30 percent).

Although the other urban sites also had very high impervious cover amounts, diazinon concentrations at these sites were not significantly higher than site 14, the reference site. One possible reason for this is there may be specific sources within sites 3 and 4 that may be consistently using diazinon, and if so, at concentrations higher than what is recommended. To more accurately pinpoint the specific source or sources of diazinon at sites 3 and 4, sampling at each storm drain inlet could be conducted. This could narrow down specific locations where diazinon is being used, which would enable outreach efforts to target those specific sources. The Alameda Countywide Clean Water Program (1999) sampled stormwater from street gutters to identify specific sources of diazinon after confirming that diazinon was being discharged to San Leandro Creek via outfalls. The results of their study showed that samples collected from certain blocks of properties contained elevated diazinon concentrations some of the time, while other samples were consistently clean.

For the three nutrients, sites 11 and 12 had concentrations significantly higher than the reference site. Sites 11 and 12 drain a large commercial tree farm that is located adjacent to the creek in the upper watershed. Nitrite and orthophosphate concentrations were highest in January and lowest in April. Nitrate concentrations were highest in April and November, although they were high in January as well. It is likely, although not substantiated that the tree farm is using fertilizers throughout the year and these fertilizers are being discharged in the stormwater runoff. It would be beneficial to determine what types and amounts of fertilizers the tree farm uses and at what times of the year so a connection could be made between specific land practices, nutrient concentration, and best management practices.

Concentration versus Imperviousness

Correlation analysis was done to determine if a relationship exists between pollutant concentration and imperviousness in the watershed. A positive correlation was found for diazinon indicating that as imperviousness increases, concentration also increases. This is likely due to the fact that diazinon is typically used in urban areas in and around households and commercial properties where high percentages of impervious surfaces exist. Imperviousness at sites 1 through 7 range from 72 to 93 percent. The high amount of impervious cover in the urbanized portion of the watershed provides a direct pathway for diazinon to be transported to the creek.

On the other hand, chlorpyrifos had a negative correlation with imperviousness, indicating that as imperviousness decreased, concentration increased. Impervious values in the upper watershed sites range from 1 to 70 percent. Site 9, although located in the upper watershed, has a percent imperviousness of 70 percent because approximately 10 acres (out of 14.7) are classified as "research centers". The negative correlation is likely a representation of the types of land uses that can be found in the upper watershed. These rural land uses have little impervious surface coverage. Chlorpyrifos may be used to control pests such as flies, termites, ants, and lice in and around horse stables and for agricultural purposes in the upper watershed. Concentrations were highest at sites 8, 12, and 13. Site 8 is dominated by "irrigated" (47 percent) and "farmsteads and other agriculture" (32 percent) land uses. Sites 12 and 13 are dominated by "herbaceous rangeland". A commercial tree farm is located at site 12 and an equestrian facility is located at site 13.

The results of this thesis indicate that high concentrations of the organophosphate pesticide, diazinon, are entering San Francisquito Creek from residential and commercial areas in the lower portion of the watershed. While chlorpyrifos is also a widely used pesticide, results indicate that land uses typical of the rural watershed may be using the pesticide more than the urban areas. Results also indicate that certain land use practices in the upper watershed are contributing significantly higher concentrations of nutrients than a relatively undisturbed site.

Recommendations

Over 500 water bodies in California, totaling over 9,000 miles of stream, creek, river, and coastal miles, are listed as impaired (U.S. Environmental Protection Agency 1999a). Improving the condition of urban creeks is important because they: 1) provide habitat for wildlife, including spawning ground for anadromous fish, 2) are an excellent resource for environmental education, 3) can be a source of municipal water, 4) provide a location for recreation, 5) provide flood protection when managed correctly, and 6) can be a central focus of the community by bringing together volunteers and committees with common goals. Although many creeks are located in urban areas, where land uses unavoidably impair water quality, it is still possible to more effectively manage the watershed to improve environmental quality.

Improving the quality of the nation's waters is a primary goal of the Clean Water Act. The Clean Water Action Plan (1998) integrates existing efforts with new action items to restore and protect water quality on a watershed basis. According to the Plan, existing programs need to be strengthened to "protect public health, enhance stewardship of natural resources, strengthen polluted runoff standards and controls, and improve information and citizen's right to know." To accomplish this, the Plan lists numerous key action items. Examples of these actions include identifying sources, transport, and impacts of polluted runoff, improving monitoring and assessment, developing incentives for reducing polluted runoff, and establishing numeric criteria for nutrients.

The data presented here will be useful for targeting specific areas in the watershed that are contributing to the impairment of San Francisquito Creek. This type of monitoring would also be useful at local, statewide, and national levels to help determine if a stream is impaired. According to Ruffolo (1999), California lacks sufficient data to determine which water bodies are clean and which are impaired thereby requiring TMDLs. By identifying the causes of water quality impairment, best management practices could then be implemented in target areas to help states improve water quality and meet TMDLs for impaired streams.

To further substantiate the findings of this research, monitoring should continue and be expanded to include other sites and more storm events. Long-term monitoring would allow comparisons to be made, which will be particularly useful when significant land use changes occur in the watershed.

However, monitoring, especially for pesticides, can be costly. This study was limited in scope due to the high costs associated with lab analysis of pesticides. Although the total cost of this study was approximately $6,000.00, in-kind services were provided by Pacific EcoRisk Laboratories to cover the cost of staff time. Without this generous donation of time, the analysis itself would have cost an additional $9,000.00. Not all pollutants are as costly to analyze. Nutrients, for example, can be done in the field and requires an initial purchase of a colorimeter. Kits to analyze specific pollutants can then be purchased as needed.

In addition to long-term monitoring, recommendations for future work include the collection of composite samples throughout a storm event, rather than just the first flush, which would be more representative of an entire storm event. Flow measurements would also be useful to calculate the load of pollutants entering the Creek.

Volunteers can be used to decrease the costs of monitoring, although chemical analysis tends to be the most costly component of a monitoring program. Even more important than cost reductions, recruiting volunteers to assist in monitoring efforts increases community involvement and education and allows citizens to become stewards of their watershed. Local agencies could also utilize volunteers to collect water quality data to reduce costs associated with staff time. However, Rigney (1993) warns that citizen monitoring may not be appropriate for enforcement, litigation, and research purposes. Rather, citizen monitoring can be used to provide baseline data and information to help decision-makers. If citizens were to be involved in monitoring for purposes associated with litigation or enforcement, careful verification of methods and results should be conducted by a professional.

Public outreach and education to both residential and commercial properties should be implemented throughout the entire watershed. Much of this education is already occurring in the municipalities in the San Francisquito Creek watershed and continued support of these programs is recommended. Education should be extended to those landowners lying outside of the urban area. Certain land uses, such as the tree farm, may need to be relocated further away from the creek to prevent significant amounts of nutrients from being discharged to the creek or, fertilizer practices could be changed to more efficient methods to contain runoff. Current practices at commercial and private equestrian facilities should be evaluated to determine what could be modified to decrease the use of toxic chemicals and thereby decrease the impacts to the creek.

Best management practices (BMPs) should be implemented to decrease the amount of runoff and therefore pollutants that actually reach the creek. The Start at the Source Manual (Bay Area Stormwater Management Agencies Association 1999) recommends an "infiltration approach" to stormwater management. This approach allows stormwater to flow slowly over pervious surfaces, such as landscaped or recreational areas. Not only does the slow flow reduce overall runoff volume, it also allows pollutants to settle into the soil. When the runoff does reach the outfall, the pollutant load has been greatly reduced. Specific approaches include, but are not limited to, infiltration basins, detention ponds, retention systems (Bay Area Stormwater Management Agencies Association 1999), and constructed treatment wetlands. Landowners should be made aware of these practices and encouraged to implement them.

In addition to BMPs, the restoration of historical wetlands can aid in mediating water flows and improving water quality. However, wetlands should not be viewed as water treatment facilities, but rather as functioning ecosystems.

Finally, from the greater land use perspective, policies that place limits on impervious cover would also contribute to reducing runoff volumes and likewise pollutant loading to streams (Mitchell 2000).

The ban on chlorpyrifos in January 2001 (U.S. Environmental Protection Agency 2000) may reduce the amount of the pesticide entering the creek; however, continued use of other pesticides such as diazinon in primarily urban areas, will continue to be a problem. In a report by the Pesticide Action Network (1999), a recommendation is made to the California Environmental Protection Agency to ban diazinon immediately so surface waters in the state will be free of the toxic chemical. Until then, educating landowners and land managers on the proper use, storage, and disposal of pesticides as well as alternative pest management techniques could contribute to the reduction of these pesticides.

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APPENDIX A

SITE NUMBER	DIAZINON CONCENTRATION (ug/l)			
	4/5/99	11/7/99	1/11/00	MEAN
one	<0.03	0.092	0.262	0.128
two	0.280	0.534	0.326	0.380
three	0.030	0.848	0.768	0.549
four	<0.03	0.890	0.754	0.548
five	0.440	0.405	0.294	0.380
six	0.030	0.290	0.113	0.144
seven	0.030	0.156	0.122	0.103
eight	0.030	0.466	0.057	0.184
nine	0.030	0.074	0.056	0.053
ten	0.030	0.174	0.106	0.103
eleven	0.030	0.083	0.270	0.128
twelve	0.030	0.062	0.055	0.049
thirteen	0.030	0.049	0.053	0.044
fourteen	0.030	0.037	0.052	0.040

SITE NUMBER	CHLORPYRIFOS CONCENTRATION (ug/l)			
	4/5/99	11/7/99	1/11/00	MEAN
one	0.0690	0.1390	0.1040	0.1040
two	0.1350	0.2510	0.1460	0.1770
three	0.1350	0.0680	0.1790	0.1270
four	0.0990	0.0625	0.1860	0.1160
five	0.0820	0.0625	0.1520	0.0990
six	0.0650	0.0625	0.0650	0.0640
seven	0.1860	0.0720	0.2100	0.1560
eight	0.1030	0.1140	0.8160	0.3440
nine	0.0510	0.0790	0.1090	0.0800
ten	0.0625	0.4220	0.2010	0.2290
eleven	0.0625	0.1760	0.0910	0.1100
twelve	0.0490	0.0625	0.9170	0.3430
thirteen	0.0625	0.0625	0.9110	0.3450
fourteen	0.0625	0.0625	0.0625	0.0630

SITE NUMBER	AMMONIA CONCENTRATION (mg/l)			
	4/5/99	11/7/99	1/11/00	MEAN
one	0.520	0.610	1.460	0.863
two	0.640	0.780	0.580	0.667
three	0.630	0.230	0.750	0.537
four	0.530	0.110	1.080	0.573
five	0.420	0.120	0.180	0.240
six	0.660	1.470	0.310	0.813
seven	0.240	0.700	0.310	0.417
eight	0.610	0.670	0.100	0.460
nine	0.170	0.680	0.540	0.463
ten	0.760	0.960	0.610	0.777
eleven	0.420	2.750	0.760	1.310
twelve	0.560	1.180	0.800	0.847
thirteen	0.140	0.130	0.130	0.133
fourteen	0.310	0.020	0.110	0.147

SITE NUMBER	NITRATE CONCENTRATION (mg/l)			
	4/5/99	11/7/99	1/11/00	MEAN
one	5.300	0.500	0.400	2.067
two	4.900	0.900	0.400	2.067
three	6.900	1.200	0.300	2.800
four	12.300	0.100	0.300	4.233
five	7.700	1.300	0.100	3.033
six	3.400	0.100	0.100	1.200
seven	4.400	0.800	0.300	1.833
eight	9.500	0.100	0.100	3.233
nine	3.500	0.700	0.400	1.533
ten	8.000	0.100	0.500	2.867
eleven	17.900	17.600	10.900	15.467
twelve	17.000	14.200	8.400	13.200
thirteen	6.100	0.200	0.300	2.200
fourteen	5.800	0.300	0.200	2.100

SITE NUMBER	NITRITE CONCENTRATION (mg/l)			
	4/5/99	11/7/99	1/11/00	MEAN
one	0.054	0.034	0.152	0.080
two	0.073	0.069	0.177	0.106
three	0.076	0.049	0.046	0.057
four	0.084	0.414	0.064	0.187
five	0.084	0.051	0.007	0.047
six	0.034	0.040	0.023	0.032
seven	0.039	0.056	0.025	0.040
eight	0.077	0.126	0.022	0.075
nine	0.032	0.065	0.055	0.051
ten	0.098	0.027	0.061	0.062
eleven	0.194	0.297	0.486	0.326
twelve	0.155	0.276	0.417	0.283
thirteen	0.029	0.017	0.021	0.022
fourteen	0.048	0.002	0.020	0.023

SITE NUMBER	ORTHOPHOSPATE CONCENTRATION (mg/l)			
	4/5/99	11/7/99	1/11/00	MEAN
one	1.640	1.480	2.750	1.957
two	1.350	1.550	1.070	1.323
three	1.010	1.680	1.940	1.543
four	1.110	1.010	2.120	1.413
five	1.400	1.680	0.490	1.190
six	0.880	2.260	1.530	1.557
seven	1.170	1.590	1.450	1.403
eight	1.420	1.650	0.530	1.200
nine	0.680	1.140	0.980	0.933
ten	1.760	0.980	1.320	1.353
eleven	6.900	26.400	33.200	22.167
twelve	4.600	29.800	31.400	21.933
thirteen	0.300	0.440	0.510	0.417
fourteen	0.980	0.420	0.330	0.577